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The Effect of Fluorine Source and Concentration on the Crystallization of Machinable Glass–Ceramics

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Abstract

Transparent and clear glasses were prepared from the MAS system (based on $MgO–Al_2O_3–SiO_2$*) with different fluorine contents. Their crystallization behaviour to giving mica glass–ceramics upon heat treatment was studied as a function of the source of fluorine and its concentration. The predominant crystalline phase in these glass–ceramics is fluoborite, norbergite, or fluorphlogopite, depending on the heat-treatment temperature, fluorine source, and concentration. An interlocking microstructure of fluorphlogopite in a glassy matrix is observed above 870°C.*

Ausgehend vom ternären System $MgO–Al_2O_3–SiO_2$ *wurden transparente und klare Gläser mit variierendem Fluorgehalt erschmolzen. Ihr Kristallisationsverhalten, das bei einer Wärmebehandlung zu einer glimmerartigen Glaskeramik führt, wurde in Abhängigkeit des Fluorgehalts und dessen Zugabeart untersucht. Die vorherrschenden kristallinen Phasen dieser Glaskeramiken sind, je nach der Temperatur der Wärmebehandlung, der Fluorquelle und des Fluorgehalts, Fluoborit (*$Mg_3[(OH,F)_3BO_3]$*), Norbergit (*$Mg_3[(OH,F)_2SiO_4]$*) oder Fluorphlogopit (*$KMg_3[(OH,F)_2AlSiO_3O_{10}]$*) Es hat sich gezeigt, daß der Fluorphlogopit in der glasigen Matrix bei Temperaturen über 870°C in einer durchgehend verbundenen Phase vorliegt.*

On a préparé des verres transparents et translucides appartenant au système MAS (basé sur $MgO–Al_2O_3–SiO_2$*) et possédant différentes teneurs en fluorine. On a étudié leur cristallisation en vitrocéramiques mica par traitement thermique en fonction de la source de fluorine et de sa concentration. La phase cristalline principale obtenue dans ces vitrocéramiques est, selon la température du traitement thermique, la source de fluorine et sa concentration, la fluoborite, la norbergite ou la fluorphlogopite. Au dessus de 870°C on observe une structure enchevêtrée de fluorphlogopite dans une matrice vitreuse.*

1 Introduction

Glass–ceramics, wherein two-dimensional mica crystals are nucleated internally and crystallized from fluorine-containing glasses have been developed.[1–4] These mica-containing glass–ceramics are unique because they possess the unusual property of machinability, that is, they can be machined to precise tolerances and surface finish with conventional metal-working tools. These materials show less sensitivity to surface damage and greater resistance to brittle fracture than do most other ceramic materials. Good machinability of the mica-based glass ceramics was attributed[1,2] to the unique microstructure of an interlocking array of plate-like mica crystals dispersed throughout a glassy matrix. The 'house-of-cards' microstructure is the key to their machinability. As with natural mica sheet, it is difficult to propagate a fracture through the thin, flat mica crystals. Typically, fractures follow the glass–matrix interfaces and cleavages planes of the mica. The microscopic fractures are repeatedly deflected, branched, and blunted; in effect, turned around and arrested.

The presence of fluorine in the base glass enhances phase separation, and phase separation usually precedes the crystallization. In the glass system of the MAS type (MAS: $MgO–Al_2O_3–SiO_2$), fluorine has the role of a nucleating agent. But the process of nucleation in glass as a function of temperature only is rather complex[2] and is not well understood.

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The objectives of the present research are:

to determine the role of the fluorine content in the process of nucleation in the base glass:

$MgO–Al_2O_3–R_2O–SiO_2–F$ (R = alkali);

to investigate the effect of the fluorine source on glass nucleation;

to investigate the effect of the fluorine source and content on the morphology developed in the glass during heat treatment;

to discuss the crystal chemistry of precipitated fluorphlogopite and the resulting properties of the glass–ceramics.

2 Experimental

For this study, glasses having weight-percentage compositions of: SiO_2 38·1; B_2O_3 11·3; Al_2O_3 16·3; MgO 21·1; K_2O 4·5; CaO 0·1; and F^{-1} were used. The F^{-1} content was changed in the range from 2·5 to 8·6. Typical batch materials employed for these glasses were: sand, alumina, calcined magnesite, potassium carbonate, and ammonium fluoride or aluminium fluoride or magnesium fluoride (Table 1). The batch ingredients were ball-milled together and thereafter melted in a closed platinum crucible for about 4–6 hours in an electrically fired furnace operating at 1420–1490°C.

The melts were poured into a steel mould to form plates 5 mm in thickness. These glass plates were immediately transferred to an annealing furnace operating at about 600–650°C.

The volatilization of fluorine from the glass melts depends on the glass composition and the type of the original fluorine compound introduced into the glass melt. Hence, in the case when NH_4F was used, fluoride volatilization was high (corrections of 50–100% wt were used) and was not reproducible for small batches. In the case when AlF_3 and MgF_2 were used, fluoride volatilization was relatively low, i.e. about 15–20% wt.

Table 1. Compositions of base glasses as-cast

Sample code	*Origin of F^{-1}*	*Fluorine content (%wt)*
M-1	NH_4F	3, 5
M-2	NH_4F	2, 6
M-3	NH_4F	2, 5
M-7	NH_4F	6, 2
M-7_T	NH_4F	7, 8
M-9_2	MgF_2	8, 6
M-9_4	MgF_2	4, 1
M-8	AlF	5, 2
M-10_T	AlF_3	6, 03

Table 2. Heat-treatment procedure

Sample code	*T_N (°C)*	*T_g (°C)*	*Appearance*
M-1	750	1 000	white
	800		translucent
	850		white
M-2	700		transparent
	750		transparent
	800	1 000	white
	850		translucent
M-3	650		transparent
	700		transparent
	750		transparent
	800	1 000	translucent
	850		white
M-7	750		translucent
	800		translucent
	850	1 000	white
M-7_T	750		translucent
	800		translucent
	850	1 100	white
M-9_2	750		transparent
	780		translucent
	800	1 100	white
	8 500		translucent
M-9_4	800		translucent
	850	1 100	white
	870		translucent
M-8	750		transparent
	800		translucent
	850	1 100	white
	870		translucent
M-10_T	750		transparent
	780		transparent
	800		translucent
	850	1 100	white

After annealing, the blocks were cut into plates of dimensions of approximately 1 × 0·5 × 0·5 cm and were carefully polished.

The preferred heat-treatment practice consists of a two-step schedule. The glass article is initially heated to a temperature somewhat above the transition range, e.g. at about 750–850°C (Table 2), and maintained within that temperature field for a sufficient period of time to ensure good nucleation and initiate incipient crystal development.

Subsequently, the article nucleated in this way is raised to a temperature between about 1000 and 1100°C and held within that temperature range for a sufficient length of time to complete substantial crystal growth. A nucleation period of about 1–5 h, followed by a crystal-growth period of about 1–3 h, has been determined and found to be very satisfactory.

As-prepared glasses were subjected to DTA to obtain the transformation temperature from the non-crystalline to the crystalline state.

The chemical compositions of the glasses and the glass–ceramics after heat treatment were analyzed by wet chemical methods. Crystalline phases were identified by X-ray powder-diffraction patterns. Microstructural characterization was performed on freshly fractured and etched (HF) surfaces by means of a scanning electron microscope.

Densities were measured by the ether-displacement method. Machinability was tested by drilling and turning.

3 Results and Discussion

Transparent, clear glasses were obtained after quenching the glass melts for all compositions. DTA curves for each glass composition showed an exothermal peak at about 750–850°C, indicating some crystallization. This temperature range was used for the nucleation study of the glass samples.

3.1 Results of X-ray diffraction

Since it is not possible to determine the optimal nucleation temperature from DTA data (exothermic peaks are rather broad), all samples were heat-treated for a temperature interval as listed in Table 2. The crystalline precipitated phase in the glass matrix was identified by X-ray-diffraction results and the microstructure obtained by scanning electron microscopy.

The temperature when the material was predominantly fluorphlogopite-nucleated was used as the 'optimal' nucleation temperature. This corresponds to the temperature when the 'house-of-cards' microstructure was developed. The specific features of the 'house-of-cards' microstructure responsible for good machinability were not taken into account (i.e. the content of mica crystals in the glassy matrix and the optimal size of crystals).

Since the fluorine content affects phase separation prior to nucleation of the crystalline phase in glass,[5] it was expected that increased fluorine content would decrease the nucleation temperature. Fluorine also decreases the viscosity of glass. However, the fluorine content seems to have a more complex role than affecting only the temperature of nucleation.

X-ray diffraction was conducted after heat treatment of glass samples with different fluorine contents. For this type of glass, NH_4F was used as the raw material for introducing fluorine into the glass. According to the diffraction data for fluorphlogopite nucleation, at least 3·5% wt. of fluorine should be present in the glass before heat treatment. At a lower fluorine content (samples M-2 and M-3), the nucleation of the crystalline phase starts at a rather low temperature, 780–800°C, and fluorborate is the primary crystalline phase. Fluorphlogopite is present only in traces. After the crystal growth at 1000°C, fluorphlogopite is the basic crystalline phase and fluorborate is dissolved, but traces of the other phases are present. The process of crystallization is bulk even though some investigators[5] find surface crystallization. By increasing the fluorine content to 3·5% wt. (sample M-1), only fluorphlogopite nucleates at a temperature as low as 750°C, and it is only the phlogopite content that increases after the crystal growth.

For a higher fluorine content (more than 6% wt.: samples M-7 and M-7_T) nucleation of samples begin at the same temperature. For the sample with a lower fluorine content (sample M-1), only nonbergite crystallizes. Fluorphlogopite is not present even in traces.

After crystal growth at 1100°C, besides the diffraction peaks for nonbergite, a few small peaks for fluorphlogopite appear. Fluorborite present in the low-fluorine-content glasses is not present in the samples with high fluorine content.

It is interesting to note that fluorphlogopite does not appear as a result of crystal transformation of fluorborite or norbergite into fluorphlogopite as reported in the literature.[3] Diffraction patterns of sample M-2 after the crystal growth show that fluorborite grows as well as fluorflogopite. At high temperature, fluorphlogopite is the prevailing crystalline phase, and traces of the fluorborate phase show that fluorphlogopite does not develop from the fluorborite transformation. Fluorborate and fluorphlogopite are found to coexist in a similar glass system.[5] According to Jung,[5] fluorborite is not stable above 900°C, but this is not in agreement with the result of the study of this (present) system.

Nonbergite, with a high fluorine content, does not transform into phlogopite with increasing temperature either. Very intensive nucleation of nonbergite resulted from the nucleation process of sample M-7. Crystal growth of the same sample at 1100°C reveals weak crystallization of phlogopite, which means that phlogopite does not precipitate after nonbergite transformation as stated in the literature.[3] On increasing the temperature, nucleated nonbergite dissolves in the glass matrix rather than transforming into phlogopite. The rather low temperature of nucleation of the crystalline phases in samples M-7 and M-7_T could be explained by the presence of a high fluorine content (a lower viscosity of glass).

X-ray-diffraction analyses of samples M-9_2 and M-9_4, containing 8·6 and 4·06% wt fluorine, respectively, were conducted, the fluorine being introduced into the glass by using MgF_2 as a raw material.

When the fluorine content in glass is high (8·6% wt), nucleation starts at a rather low temperature, as low as 750°C, but only nonbergite is precipitated. By increasing the temperature of nucleation, the nonbergite content decreases, and phlogopite increases. At 850°C, both phases coexist. It seems that selaite is present in traces. The process of nucleation in glass is very similar in sample M-9_4 with 4·06% wt fluorine content and sample M-1 with 3·5% wt fluorine content. Nucleation starts at above 800°C, and phlogopite is precipitated with traces of selaite. But the crystalline forms of phlogopite in these glasses are not the same. This is difficult to explain because the difference is just that different raw-material sources are used to introduce fluorine into the glass, i.e. NH_4F and MgF_2. After crystal growth at 1100°C, in both cases (samples M-9_2 and M-9_4), phlogopite is the prevailing crystalline phase.

The process of crystallization of glass samples containing fluorine from AlF_3 as raw material, M-8 and M-10T (fluorine content 5·2 and 6·03% wt, respectively), is rather unusual. The high fluorine content in these samples is expected to result in a low nucleation temperature, but, on the contrary, nucleation is negligible below 850°C. Even nonbergite, as in M-9_2 and M-7, does not precipitate at lower temperatures. The reason for nucleation beginning at this high temperature is not obvious.

These differences could result from the different composition of phlogopite formed at 850°C, and one can only assume that the solubility of AlF_3 is rather low at this temperature.

Even though the fluorine content in sample M-10T is higher than that in sample M-8, nucleation is more intensive in sample M-8. In the process of crystal growth, only phlogopite grows. The crystalline form of phlogopite developed at 850°C is exactly the same as that reported in ASTM Card 16-352, and the phlogopite grown at 1100°C is also the same as that given in ASTM Card 16-344. Apart from the nucleation temperature and the fluorine content in glasses, the nucleation mechanism also depends on the source of the fluorine (NH_4F, MgF_2 or AlF_3). For example, samples M-7 and M-10T contain the same quantity of fluorine but from different sources. These samples show remarkable differences in the process of their nucleation. In sample M-7, nonbergite nucleated at 750°C, but in sample M-10T there was no nucleation at all at that temperature. At 850°C, nucleation of phlogopite occurred in sample M-10T, whereas, in sample M-7, nonbergite was the prevailing crystalline phase at the same temperature and phlogopite was present in traces only. Whatever the reason for this behaviour, it can have significant practical importance, such as in the case when one wants to have only phlogopite as the crystalline phase, as in machinable glass–ceramics. In order to avoid the presence of other crystalline phases apart from phlogopite, one should use AlF_3 as the raw-material source or use a high temperature of nucleation.

3.2 Results of electron-microscopy study

The general conclusion of the electron-microscopy study of the process of crystallization in these compositions is that 'the house-of-cards' microstructure is developed only when the basic crystalline phase is phlogopite. Figure 1 shows the micrographs for samples M-1, M-2 and M-3. A typical fluorphlogopite microstructure is observed only in sample M-1 with 3·6% wt fluorine. A low content of fluorine, as in sample M-2, does not show surface crystallization (Fig. 1(c)) but shows bulk crystallization. A high fluorine content, as in sample M-7 (Fig. 1(d)), does not show a typical fluorphlogopite microstructure after nucleation at 780°C. This corresponds to the result from X-ray diffraction.

Figure 2 shows the microstructures of samples M-9_2 and M-9_4 after heat treatment. Sample M-9_4 shows the typical interlocking microstructure of fluorphlogopite after nucleation and crystal growth (Fig. 2(a), (b)).

After nucleation at 800°C, only the nonbergite microstructure is observed (Fig. 2(d)) in sample M-9_2 with a high fluorine content, and phlogopite appears after growth (Fig. 2(d)).

Figure 3 shows the microstructures of samples M-8 and M-10T. It is obvious from Fig. 3 that the microstructures of samples M-8 and M-10T are not the same, even though the crystalline phase present in both samples is fluorphlogopite. Phlogopite crystals nucleated at 850°C in M-10T have different aspect ratios from those in sample M-8. Small differences in fluorine content in these samples seem to be the reason for the different rates of nucleation.

After the crystal growth at 1100°C, the phlogopite crystals developed in M-8 and M-10T have different morphologies (Fig. 3(b), (d)). The mechanism of nucleation and crystal growth is also different according to the X-ray and electron-microscopy results.

3.3 Some physical properties

Densities of as-prepared glasses were about 2·61 g/cm^3. Changes in density of the glass–ceramics heat-treated at 700–1200°C for two hours are shown in Fig. 4 for sample M-9_4.

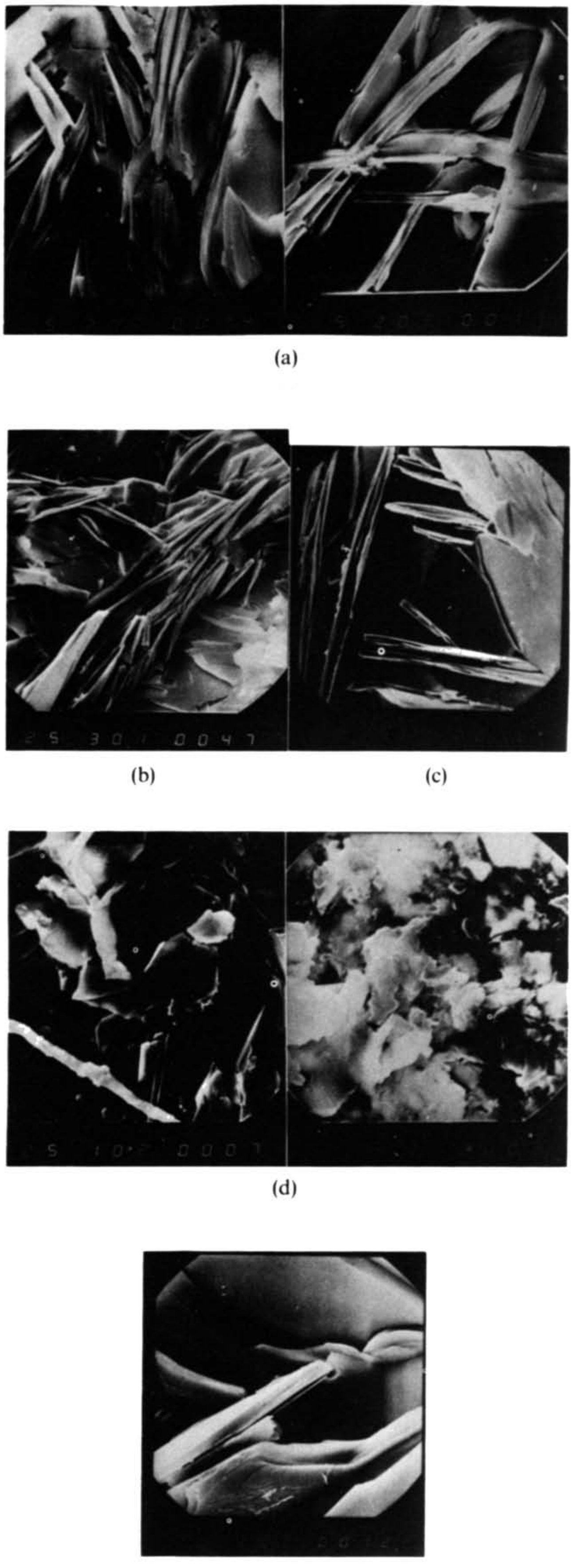
(a)
(b) (c)
(d)
(e)

Fig. 1. Mode of crystallization of the samples after heat treatment at: (a) M-1, 850°C; (b) M-1, 850–1100°C; (c) M-2, 800°C; (d) M-7, 780°C; (e) M-7, 750–1100°C.

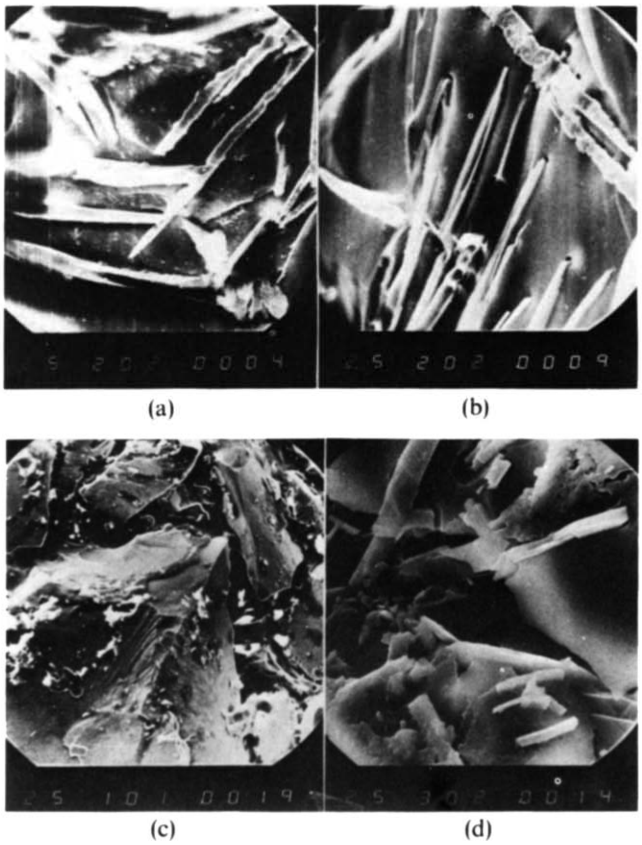
(a) (b)
(c) (d)

Fig. 2. Mode of crystallization of samples M-9_2 and M-9_4 after heat treatment at: (a) M-9_4, 800°C; (b) M-9_4, 850–1100°C; (c) M-9_2, 800°C; (d) M-9_2, 850–1100°C.

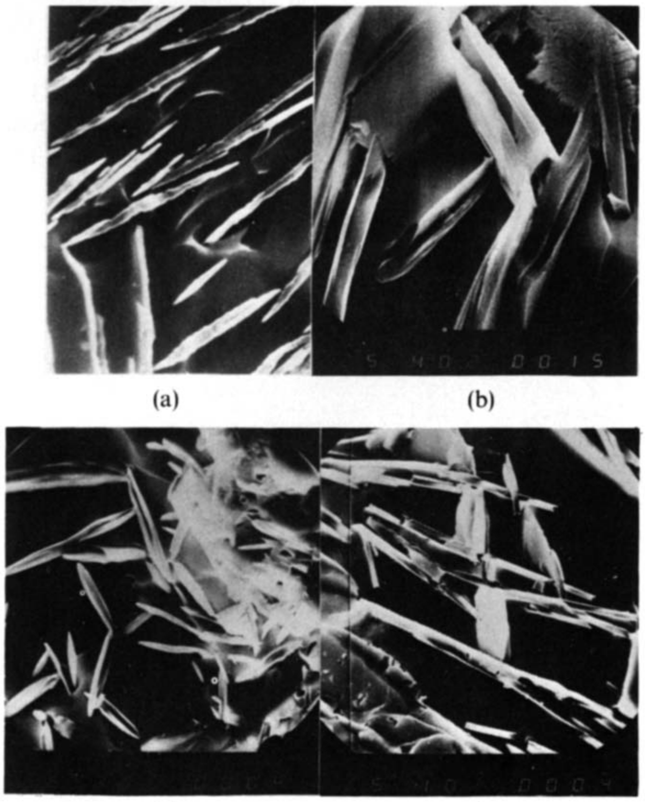
(a) (b)
(c) (d)

Fig. 3. Mode of crystallization of the samples after heat treatment: (a) M-8, 850°C; (b) M-8, 850–1050°C; (c) M-10T, 850°C; (d) M-10T, 850–1100°C.

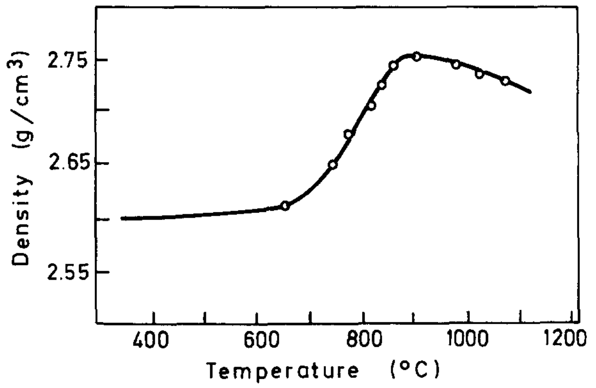

Fig. 4. Changes in density of sample M-9_4.

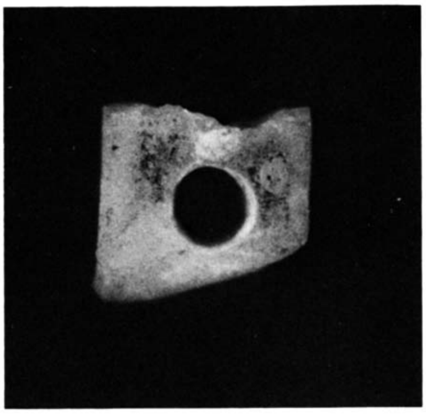

Fig. 5. Drilled fluorphlogopite glass–ceramics, sample M-9_4.

An increase in density was observed at the temperature at which the first crystalline phase was detected. That temperature depends on the nucleation temperature, which is a function of composition, as shown by the X-ray-diffraction study. The maximum density was obtained at about 870°C for all the samples that were nucleated at high temperature. After the maximum value, the density decreases with increasing temperature. The decrease in density may be attributed to the decomposition of fluorphlogopite and propagation of cracks into interlocking mica crystals accompanied by (crystal)/(propagated cracks) growth. This obviously led to the changes in microstructure, as already shown in Fig. 3(a) and (b). Figure 5 shows examples of drilled and cut samples.

It may be concluded that good machinability is obviously related to the interlocking fluorphlogopite crystals formed in the glass–ceramics, since drilling is not possible in the cases when other types of microstructure were developed in heat treatment of the glasses.

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