Oriented mica glass-ceramic by extrusion and subsequent heat treatment

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Glass-ceramics with oriented mica crystals have been produced by extruding a fluorophlogopite glass and subsequent thermal treatment. During extrusion predominantly the intermediate phase norbergite (Mg3F2SiO4) and besides small quantities of phlogopite mica crystals (Na/KMg3Si3AlO10F2) crystallized. Heat treatments at temperatures around the maximum crystallization rate resulted in an oriented crystallization of phlogopite as proved by electron microscopy and XRD analysis. The plate-like crystals are aligned with their basal planes parallel to the direction of extrusion. The degree of orientation was studied by X-ray pole figure measurements. The (003) planes show strong ring-fibre texture. The degree of orientation decreased if the crystallization was realized at lower temperatures and lower crystallization rates. The alignment mechanism is discussed.

1. Introduction

The mechanical properties of glass-ceramics mainly depend on the properties of the crystalline phase dispersed in the glassy matrix. Mica glass-ceramics, in particular of the phlogopite system, impart excellent machinability, due to the layered atomic structure of the sheet silicates which causes a basal cleavage along the (001) planes of the plate-shaped crystals. Drilling, milling or turning on a bench with convenient metal tools is possible [1].

Other mechanical properties such as bending strength and fracture toughness are considered as good, because of the high fracture energy of phlogopite crystals [2]. By orienting the crystalline phase mica glass-ceramics should exhibit anisotropic properties. An improvement of the mechanical properties in one direction is to be expected by alignment of the phlogopite plate as shown in oriented glass-ceramics of the lithium disilicate system [3]. The mechanical deformation at temperatures above the glass transformation temperature is an approved method to generate preferred orientation glasses and to produce anisotropic glass-ceramics. Two basic types of methods to obtain alignment by deformation are distinguished: first, crystal growth during deformation and direct orientation of the crystalline phases; second, deformation of glass without crystal growth, subsequent heat treatment results in an oriented crystallization [4].

Grossman [5] obtained anisotropic fluoromica at fluoroamphibole glass-ceramics by high-stress compressive deformation such as pressing, rolling or drawing. Oriented crystallization occurred both during deformation and subsequent heat treatment. Ashbee [6] extruded glasses from the lithium disilicate, fluoroamphibole and fluorophlogopite systems through opposed dies at crystallization temperatures.
Experiment work

1. Materials and extrusion

The glass used for extrusion had the following composition (in mol\%): 54SiO₂, 10Al₂O₃, 11MgO, 18F, 1Cl, Na₂O, 3K₂O. Glasses from the same system have been studied by Höland et al. [10]. Figure 1 shows a schematic drawing of the crystal formations in the glass as reported in the literature [11]. After melting and casting, the glass exhibits phase separation due to the formation of fluo-

cerolite and norbergite-rich droplets in the silica matrix. The intermediate phase norbergite crystallizes inside the droplets at temperatures above 750°C. At temperatures above 800°C fluorophlogopite starts to grow, while nor-

gite dissolves. In the chosen glass composition, nor-

gite serves as a fluorine reservoir for the formation of fluorophlogopite and not as a nucleating agent [10].

Phlogopite of symmetry 1m (monoclinic) crystallizes in plate-like morphology and is thermodynamically stable in the glass until 1220°C. Its aspect ratio depends on the crystallization temperature. To produce the glass, the raw materials were melted in a platinum crucible at 1590°C for 90 min and then fritted in water. After remelting at 1580°C, the glass melt was cast into cylindrical graphite moulds of 34 mm in diameter. After cooling from 680°C (Tg) to room temperature with 3 to 5 K/min, the glass cylinder was cut into several pieces and placed into the extruder, preheated to the treatment temperature of 820°C. The extrusion apparatus and procedure have previously been described by Roeder [12]. The parameters of extrusion are shown in Table 1. The extrusion was started after soaking the glass for about 20 min to establish temperature equilibrium. It was carried out at a viscosity of about 10⁶ dPas applying the direct extrusion technique. It was performed at pressures between 57 and 63 MPa, using a die of 8 mm in diameter and 5 mm in length. Because of the electrodegraphite die, friction effects and the die swell phenomenon did not occur [13]. A glass rod of 8 mm in diameter was obtained.

2.2 Characterization techniques and thermal crystallization

The microstructure of the extruded glasses, regarding immiscibility, nucleation and crystallization was studied using a transmission electron microscope (TEM, BS 540, Tesla, Brünn (CZ)) and a replica preparation technique [14]. The extruded glasses were heat-treated to produce a mica glass-ceramic. Thermal crystallization was realized between 800 and 1100°C using a heating rate of 120 K/min. The soaking time was varied in that manner that comparable crystal volume fractions were obtained. The microstructure of the glass-ceramic rod was studied using a scanning electron microscope (SEM, DSM 940A, Carl Zeiss, Oberkochen (Germany)). Crystalline phases were analyzed using X-ray diffraction (XRD, D 5000, Siemens, München (Germany)) in the 2θ range of 8° to 62° with a step size of 0.02° and a counting time per step of 20 s. For the qualitative determination of orientation, bulk XRD samples were cut both parallel and perpendicularly to the rod axis and subsequently polished. The indication of (hkl) reflections was realized using a scanning power diffractometer type XPert (Phillips, Kassel.

<table>
<thead>
<tr>
<th>Extrusion parameters</th>
<th>glass composition</th>
<th>extrusion temperature</th>
<th>extrusion pressure</th>
<th>extrusion velocity</th>
<th>extrusion ratio</th>
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<tr>
<td>extruded material</td>
<td>820°C</td>
<td>57 to 63 MPa</td>
<td>2 to 5 mm/min</td>
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<td>19.1</td>
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Figure 1. Schematic drawing of crystal phase formation in the glass composition used.

Table 1. Extrusion parameters
3. Results

3.1 Microstructure of the extruded glasses

The extruded glasses are homogeneous over the entire length of the rod and show light opalescence, attributed to crystallization during extrusion. Cross-sections parallel and perpendicular to the extrusion direction were analyzed by XRD (figure 2). Norbergite (JCPDS file 11-686 [15]) was detected right from the beginning of the rod. The low intensities of the reflection peaks are attributed to the low crystallinity of the samples. Both cross-sections (curves 1 and 2) show identical XRD patterns. The formation of phlogopite during the extrusion procedure, however, was not detected by XRD analysis.

In figure 3, a typical TEM micrograph of the fracture surface of an extruded glass broken parallel to the rod axis and etched using a 50:50 mixture of 5% HF and 5% HNO₃ for 2 s is shown. Spherical crystals of 50 nm in diameter can be observed. By analogy with former investigations [10] and the XRD patterns shown in figure 2, this phase is attributed to norbergite crystals, which occupy about 30% of the volume. In figure 3, an other crystalline phase possessing different morphology is also shown. Those rectangular crystals with a long axis of up to 300 nm and a short axis of about 80 nm (aspect ratio 4:1) are scarcely observed all over the rod of the extruded glass. In former studies this morphology was reported to be characteristic for phlogopite crystals. The amount of these crystals, however, is too low to be detected by XRD analysis. The occurrence of orientation of the phlogopite phase after extrusion cannot unequivocally be proved by TEM studies only.

3.2 Microstructure of the glass-ceramics

Samples of the extruded glass were crystallized by different thermal treatments as described in section 2.2. Figures 4a and b show SEM micrographs of a crystallized extruded glass heat-treated at 1100°C for 10 min, cut parallel and perpendicularly to the extrusion direction respectively. Only rectangular and hexagonal crystal characteristic for phlogopite can be observed. Their aspect ratio was determined to be 8:1. In figure 4a, a orientation of the crystals is clearly visible. The plate like crystals are aligned parallel to the extrusion direction. By contrast, crystals of the sample cut parallelly to the extrusion axis appear randomly oriented forming the characteristic house of cards of phlogopite crystals (figure 4b). However, in this section basal planes of phlogopite cannot be observed. Figure 5 shows SEM micrograph taken from the area close to the rod surface of a sample cut parallel to the extrusion axis. A orientation of the phlogopite plates both parallel to the extrusion direction and parallel to the surface was observed, indicated by the parallel arrangement of the plates and the missing basal planes of mica crystals.

XRD patterns of these samples are shown in figure 6. In the XRD pattern of the sample cut parallel to the rod axis, all reflections were detected (see curve 2). Comparison, in a powdered sample (curve 3) of the same glass-ceramic, the (001) reflections, corresponding to the basal planes of the plate-like crystals, are strongly increased (curve 1). On the other hand, in the sample cut perpendicularly to the rod axis (curve 1) the (001) reflections are either totally missed (e.g. (003) and (005)) or very weak (e.g. (001)). However, this sample shows accentuated reflections from (hk0) planes. Weak reflections were also detected from the (131) and (201) planes.

A pole figure, shown in figure 7, was obtained from the sample heat-treated at 1100°C and cut parallelly to the rod axis. The (003) reflection peak from the bus...
figures 4a and b. SEM micrographs of a polished and etched surface, detected a) parallel and b) perpendicularly to the extrusion direction of extruded glass crystallized at 1100°C for Dmin.

lane of phlogopite was chosen for measurement. The intensity of this peak decreases strongly by tilting the sample perpendicularly to the extrusion axis. The angular spread of the basal plane orientation with respect to the extrusion axis is ±14° measured as the angular width of half maximum count rate.

Samples of the extruded glasses were also heat-treated at temperatures below 1100°C, but still in the area of crystal growth of phlogopite. Figure 8 shows XRD patterns obtained from samples cut perpendicularly to the rod axis and heat-treated at temperatures between 800 and 1100°C. With increasing temperature, a lowering of the intensity of the (001) peak is observed, whereas those of the (020) and (110) reflections are increasing. Figure 9 shows an SEM micrograph of an extruded glass crystallized at 900°C for 1 h. The section parallel to the rod axis is shown. The alignment of the crystalline phase in direction of extrusion is of a much lower degree by comparison with the sample treated at 1100°C.
4. Discussion

4.1 Conversion of extruded glass into oriented glass-ceramic

Norbergite crystallizes in the above-described fluorophlogopite-based glass melt during extrusion at 820°C. It was detected both by XRD and TEM studies (figures 2 and 3). Due to its spheric morphology, no alignment of the norbergite crystals was obtained. Also fluorophlogopite was formed during the extrusion process. Because of the low amount of crystalline phase, an orientation of phlogopite crystals is not proven definitely. Thus, the extruded glass shows no clear evidence of crystal alignment.

Heat treatments at 1100°C resulted in the dissolution of the intermediate phase norbergite, while fluorophlogopite crystals grew oriented. The basal planes of the plates are oriented parallel to the extrusion direction as shown in figure 4a. The XRD pattern (figure 6, curve 2) of an oriented glass-ceramic cut parallel to the rotation axis contains the reflections of all (hkl) planes, those from (001) planes, however, accentuated. By contrast XRD patterns recorded from samples cut perpendicularly to the extrusion direction exhibit predominantly reflections from (hk0) planes. The (001) reflections do not appear on such cross-sections in highly oriented sample. This is due to the fact that crystal alignment extends only along one common axis. The c-axes of the oriented mica plates are situated perpendicularly to the extrusion direction, characteristic of ring-fibre texture, as shown in figure 10 [16]. Due to this type of orientation, the characteristic house of cards, formed by randomly oriented phlogopite crystals, is observed transversal to the extrusion axis (see figures 4b and 10). However, all basal planes are turned out and lie perpendicularly to the cross-section. Hence, the decreasing intensity of the (001) reflection peak of samples cut perpendicularly to the extrusion direction is a measure of the degree of anisotropy of this glass-ceramic. As shown in figure 8, extruded glasses crystallized between 800°C (curve 4) and 900°C (curve 3) exhibit crystal orientation, illustrated by their lower (001) reflections compared to the XRD patterns of the powder shown in figure 8, curve 5. By the relatively high intensity of the (001) reflections, however, indicate a comparably low degree of alignment. Highly anisotropic phlogopite mica glass-ceramic was produced by thermal crystallization between 1000°C and 1100°C. The high alignment of crystals is indicated by the almost vanished (001) reflection and the strong intensity of the (hk0) reflections on such cross-sections.
In the present study, the small amount of phlogopite in the extruded glass gives a hint at a presumable nucleation of phlogopite during extrusion. Oriented nuclei aligned by shear flow in the extrusion container or within the die channel may be the origin of the oriented crystals grown during heat treatment. On the other hand, anisometric structural flow units can be responsible for the oriented growth of the mica crystals. Brückner [18] first described these amorphous structural fragments, such as chains or disks, which are suggested to cause oriented crystallization of lithium disilicate in glasses deformed mechanically [3 and 19]. The fact that the degree of orientation is lower if the extruded glass is heat-treated at temperatures up to 900°C and low crystallization rates is attributed to relaxations, thermal movement and diffusion, which rearrange and destroy the preferred orientation of the glass. On grounds of similar experiments, Durschang et al. [3] propagated the non-nuclei orientation mechanism for lithium disilicate glasses, because the probability of structural rearrangement of aligned flow units is higher than of aligned nuclei. In the present study none of both orienting mechanisms, nuclei or non-nuclei, can be excluded.

At higher temperatures the disordering effect can be stronger, caused by the lower viscosity. However, with increasing temperature also the crystallization rate increases. Fast crystal growth may reduce and prevent structural rearrangement and disordering of once oriented structures. Possibly, anisometric structures of large size in a highly viscous fluid can hardly be moved from their position by thermal energy. It is also known that the aspect ratio of the a- or b-axis to the c-axis of the phlogopite plates depends on the viscosity of the melts. Thus, the higher the crystallization temperatures the higher is the aspect ratio obtained. In the present study, the aspect ratio was determined to be 4 at 900°C (figure 9) and to be 8 at 1100°C (figures 4a and b). A faster crystal growth occurs at higher temperatures along the a- and b-axes, which coincides with the direction of extrusion. Both effects, the high crystallization rates and the preferred crystal growth in direction perpendicular to the basal planes, producing the higher aspect ratio, are suggested to cause the higher degree of oriented crystals at high temperatures. At temperatures above 1000°C these effects are strong enough that nearly all crystals are growing faster in the direction of extrusion than the preferred orientation in the glass or the alignment of nuclei is lost.

5. Conclusions

This study shows that it is possible to achieve oriented mica glass-ceramics by extruding glass and subsequent heat treatment. The extruded glass contains randomly oriented norbergite crystals and a small amount of fluorophlogopite. The subsequent glass-ceramic consists of about 40 vol.% plate-like fluorophlogopite crystals, showing a high orientation with their basal plane parallel to the extrusion axis. The alignment is attributed to
oriented nuclei and/or oriented anisometric structural flow units, which grow especially at temperatures above 1000°C with high crystallization rates in the direction of extrusion. Lowering the crystallization temperature decreases the degree of orientation.

Further investigations will apply this method to other mica-based glass systems and show the resulting mechanical properties and the influence on the extrusion process parameter on the resulting glass-ceramics. Studies on the structure of extruded glasses are expected to clarify the alignment mechanism.

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6. References


