Crystallization of mica in the $K_2O-SiO_2-MgO-MgF_2$ glass system

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Abstract. The growth of crystalline mica in $K_2O-SiO_2-MgO-MgF_2$ glass has been studied and characterised through various techniques, viz. differential thermal analysis (DTA), X-ray diffraction (XRD), microscopy (SEM), and microhardness tests. It is observed that the addition of titania has a stronger influence on the growth of mica crystallites as compared to variation in heat treatment schedules.

Keywords. Glass-ceramics; mica growth; crystallization of mica.

1. Introduction

Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of glass through regulated heat treatment schedules. They are distinct from traditional ceramics in that the crystalline component is internally produced within the glass. As the parent glass is usually made of multicomponent oxides and some fluorides, several crystalline phases could evolve within the glass system. By exercising a proper choice of composition, additive agents and heat treatment schedules, preferential growth of crystallites of the desired size and shape is attained with the required physical, chemical and mechanical properties.

A glass-ceramic, which is machinable with conventional metal working tools is advantageous for machining parts or components to tight tolerance. Mica based glass-ceramics are machinable, strong, fracture resistant, thermal shock resistant and have good dielectric properties (Beall 1971). Mica is a sheet-structured silicate, which cleaves along the 001 plane but exerts a strong resistance in the perpendicular direction. A microstructure consisting of randomly oriented interlocking microcrystallites is helpful in deviating and arresting microfractures. Machinability is a result of localized granulation. This paper reports the influence of heat treatment and TiO_2 additive on the growth of crystalline phases and their relative advantages in the development of a mica-based machinable glass-ceramic.

2. Glass melting

The compositions chosen for study were similar to that by Grossman (1972) viz. K_2O 11, SiO_2 62, MgO 16.4, MgF_2 10.6 (composition C1) and K_2O 13.5, SiO_2 60.5, MgO 13.5, MgF_2 12.5 (composition C2) all in wt%. Titania was added from 2 to 13 wt% to the batch composition. Several batch compositions of about 100 g were melted at 1450–1480°C for 2–6 h and poured into steel moulds or quenched in water.

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A clear or opalescent glass was obtained depending upon the mode of quenching. The glass of composition with 13% titania was blue in colour and bears the prefix 'B' in the tables. Similarly transparent glass has a 'T' and opalescent glass an 'O' as prefix.

3. Results

3.1 Differential thermal analysis

DTA measurements of the quenched and heat-treated glass powder were taken. The rate of heating was 15°/min. Figure 1 shows several exothermic peaks indicating the occurrence of crystalline phases in the range 950 to 1300°C, approaching the melting point of the batch. After heating at 1000°C for 2 h, exothermic peaks were few and some endothermic peaks at 1180 and 1250°C corresponding to the melting of tetrasilicic mica, magnesium flouride or forsterite were seen.

Figure 1. Differential thermal analysis in (a) C2 glass and (b) heat-treated C2 glass.

Table 1. Effect of titania (2 wt%) on the formulation of mica.

Material code	Heat treatment temperature (°C)	Major phases*
C2-A	rt—700/1 h—1050/3 h	M:E as 3:1
C2-TA	rt—700/1 h—1050/3 h	M:E as 4:1
C2-B	rt $\xrightarrow{15^\circ/\text{min}}$ 650 $\xrightarrow{1^\circ/\text{min}}$ 750/1 h $\xrightarrow{5^\circ/\text{min}}$ 1100/2 h	M:E as 3:1
C2-TB	rt—650—750/1 h—1100/2 h	M:E as 4:1
C2-C	rt—600—720/1 h—1150/1 h	M:E as 3:1
C2-TC	rt—600—720/1 h—1150/1 h	M:E as 4:1
C2-D	rt—600—740/1 h—1100/1 h	M:E as 3:1
C2-TD	rt—600—740/1 h—1100/1 h	M:E as 4:1

*M — $KMg_{3.25}Si_{3.625}O_{10}(OH/F)_2$ —(26–1321) mica; E — $MgSiO_3$ enstatite (19–768).

3.2 Heating schedules

A three-step heating schedule has been adopted for annealing, nucleating and growth of the crystallites. Observations showed that the glassy phase alone could be detected on annealing at 600 to 650°C for durations up to 24 h. The second step for improving nucleation density had varied schedules. Table 1 shows glass of composition 2 (C2), with a slow heating second step (1°/min) from 600 to 720–750°C. The third step is for the growth of crystallites at temperatures varying from 1000 to 1150°C.

3.3 Density

The density of the glass chunks was between 2.52 and 2.53 g/cm³. After heat treatment, it ranged from 2.62 to 2.68 g/cm³. The change in density on going from glass to a glass-ceramic in this case was about 5%.

3.4 X-ray diffraction

XRD has been used for the identification of crystalline phases. The multiple phases were resolved by comparing data from differently heat-treated specimens. The diffraction patterns taken after the final heating step showed that mica and enstatite crystallites formed in the ratio (calculated from peak intensities of strong characteristic lines) as shown in tables 1 and 2. In table 2 the first two steps of heating were identical. The duration of heating in the third stage was varied. There was little change in the phases formed except that for prolonged heating forsterite lines appear. Table 1 shows also that a small addition of 2% by wt. of titania results in enhanced formation of the mica phase, more effectively than heat treatment variations. The average crystallite size was in microns and did not influence measurements. Figure 1 shows the exothermic peaks in DTA due to crystallization of glass on heat-treatment. The peaks are due to crystallization of phlogopite, enstatite, forsterite and other silicates.

3.5 Microhardness

Microhardness measurements were carried out on polished materials with Knoop and Vickers diamond indenters. For loads below 100 g hardness numbers were higher but did not vary much for loads in the range 100 to 300 g. In general, 10 to 20 impressions are taken depending on the scatter of impression diagonal values and distortion of impression, if any. In titania-doped BC22 some impressions averaged around a different hardness value 311 kg/mm^2 . The microhardness values do not seem to change much as seen from table 3 between glass and glass-ceramic when enstatite or forsterite phases are formed but they do relate to density.

3.6 IR spectra

FTIR spectra were used to complement information on crystalline phases obtained from XRD. The vibrational modes confirmed the molecular units (Nakamoto 1986).

Table 2. Evolution of phases and density change with heat treatment.

Material	Heat treatment temperature (°C)	Density (g/cm ³)	Phases*
C2z'	C2z—600/15 h	2.53	Glass
C2z'A	C2z'—800/0.5 h—1150/9 h	2.653	E and M
C2z'B	C2z'—800/0.5 h—1150/12 h	2.657	E and M
C2z'C	C2z'—800/0.5 h—1150/24 h	2.662	E, M and weak forsterite

*M — $\text{KMg}_{3.25}\text{Si}_{3.625}\text{O}_{10}(\text{OH/F})_2$ —(26–1321) mica; E — MgSiO_3 enstatite (19–768).

Table 3. Density and microhardness changes with heat treatment.

Material	Heat treatment temperature (°C)	Density (g/cm ³)	H (P = 100 g) (kg/mm ²)	Phases
TC2	600/1 h	2.52	578 ± 15	Glass
TC22	TC2—1100/4 h	2.62	580 ± 15	Enstatite
OC2	600/1.5 h	2.53	576 ± 15	Glass
OC22	OC2—950/6 h	2.63	568 ± 10	Forsterite
BC2	650/1 h	2.53	598 ± 15	Glass
BC22	BC2—950/6 h	2.62	311 ± 10	Phlog.
			590 ± 15	Enstatite
C2X	600/5 h	2.46	576 ± 30	Glass
C2X2	C2X—1150/2 h	2.68	680 ± 30	Enstatite, forsterite
C2Z	600/15 h	2.53	610 ± 21	Glass
C2Z2	C2Z—1150/9 h	2.65	675 ± 20	Enstatite, mica

3.7 Microstructure

The micrographs of the fractured surface are shown in figures 2 and 3. After the heat treatment at 720 to 750°C some features were discernible in SEM. Glass-in-glass phase separated droplets were seen for both compositions 1 and 2. In C2 to which 2 wt% titania was added the droplet sizes were small. Spherulitic growth and mica flakes could also be seen. When titania was 13 wt% crystallites were fine with a different morphology. EDX counts indicated that droplets were rich in potassium and low in magnesium as compared to the matrix though both contained the same ions viz. Si, Mg and K (also Ti in doped compositions).

4. Discussion

The volume changes on going from glass to a glass-ceramic are due to differences in density of the glass and crystalline phases. The change was found to be 5%, which shows that shrinkages involved on heat treatment of glass are low and articles could be made to tight tolerance.

The micrographs in figure 2 show phase separated droplets. The droplets were bigger as expected when fluorine is present (Hinz 1977). Average size was 2 μm for composition 1 and 0.7 μm for titania-added composition 2. With further heating the droplets disappear and spherulitic growth of crystallite is observed. The micrographs show that droplets disappear when crystal growth starts, implying initial nucleation within droplets. We observed that even a rough surface can induce crystallization (McMillan 1979). Volume rather than surface crystallization is desired in a glass as the former alone introduces homogeneity and strength in a material.

A glass-in-glass phase separation usually precedes nucleation and occurs while cooling the melt or in the first annealing stage of the glass. Further heating results in the formation of nuclei either in the droplets or in the matrix either through homogeneous or heterogeneous nucleation. Homogeneous nucleation has the maximum density, normally at a temperature close to the glass transition temperature, which was 600°C in our composition. But detectable crystallinity occurred only above 750°C. A slow rate of heating for the second stage was chosen to improve nucleation density. Table 1 shows that mica formation was influenced much more by titania addition than by heat-treatment variation at the nucleation stage. The micrographs in figure 2 show that mica crystallites are finer in size and homogeneously distributed when TiO_2 is added. The crystalline phase is not that of tetrasilic mica but is a solid solution, an off-stoichiometric mica phase, $KMg_{3.25}Si_{3.625}O_{10}F_2$. Some residual glass phase is also present. When there was fluorine loss due to long-duration heating forsterite formed instead of mica.

An additive like titania enhances phase separation and provides substrates for bulk nucleation. Phase separation is conducive to nucleation and crystal growth as the interface energies are lowered. Dalal and Davies (1977) studied tetrasilic mica-based compositions of glass in which phase separation arose either due to low solubility of MgF_2 in the melt or due to shift in coordination number of Mg ions from four to six while cooling. A similar separation can occur when titania is present in the compositions (Stookey 1960). At high temperatures Ti can replace Si in the network but at lower temperatures the stable coordination number six is preferred. It is

Figure 2. Electron micrographs of the fractured surface showing (a) droplet phase and (b) spherulitic crystal growth.

Figure 3. Growth of mica crystallites without (a) and with (b) titania.

achieved either by attracting non-bridging oxygens or by combining with a divalent ion to form a titanate. We have observed the presence of magnesium titanate when titania content was high, 13 wt%. The crystallites of insoluble material or titanate separating out could act as nuclei for further crystal growth. As TiO_2 (rutile) has the same structure as MgF_2 epitaxial growth is also likely with either of them acting as nuclei. Chondrodite or norbergite, which form at 800°C through solid state reaction, can also act as substrates as there is structural compatibility between sellaite (MgF_2), chondrodite ($2\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$), norbergite ($\text{Mg}_2\text{SiO}_4 \cdot \text{MgF}_2$) and fluorphlogopite.

The role of additive in nucleation and crystallization has been discussed by James (1982). They influence the kinetics of phase separation and/or shift the immiscibility boundary. We inferred earlier (Saraswati 1990) that free energy, interface energy and diffusion parameters are affected resulting in changes on nucleation and crystal growth owing to change in viscosity. On comparing XRD and SEM EDX at various crystal sites it was not obvious whether titania or titanate acted as substrates. But they do enhance the growth of the mica phase by suppressing the enstatite phase.

Microhardness numbers reflect on the resistance to plastic deformation. If the load is less the penetration depth of the indenter would be small. In a glass melt the surface tends to be richer in silica, unless care is taken to homogenize the melt. Second, if surface crystallization takes place, the values may not be representative of the bulk. In our samples load was kept at 100 g and the hardness numbers were found to change with density, which is a bulk property. We can safely say that the hardness values shown in table 3 reflect on the glass or crystalline phases in the bulk. There is not much difference between the glass and glass-ceramic with enstatite or forsterite phase because of similar bonding in the molecular units. In BC22, with 13 wt% titania, an average around 311 kg/mm^2 could indicate clusters of mica crystals.

5. Conclusions

From our results it is possible to conclude that phase-separated droplet sizes are influenced by the presence of fluorine and titania. The growth of fluor mica phase and crystallite morphology are influenced by the presence of titania. Heat treatment schedule variations have comparatively less influence as compared to an additive like titania owing probably to the dominance of interfacial properties over diffusion.

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