New teeth for old

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There is an ever-increasing demand for long-lasting dental restorations, partly because people retain their natural teeth until later life and partly for cosmetic reasons. This demand, together with the health and environmental problems associated with mercury-based fillings, has resulted in a need to produce new, durable and aesthetically acceptable materials for use in dentistry. As part of this search for new materials we have been examining crystallisation in novel mica based glass-ceramics using kinetic neutron diffraction. We have characterised the phases formed during several different processing routes and have shown, for the first time, that, when following the "optimum" processing route, the glass crystallises not into the normal 1M mica structure but into the 2Or mica polytype. At high temperatures this phase transforms into the 1M mica phase.

The development of dental CAD-CAM systems that allow the fabrication of aesthetic all-ceramic restorations in a single visit has meant that machining processes, and the development of machinable materials have become extremely important in restorative dentistry. Mica based glass-ceramics were developed in the 1970s by Corning for CAD-CAM machined cores [1], which were overglazed to produce crowns. However, the cost of CAD-CAM systems and the related technology was too expensive to be used routinely. Recently however, there has been a reduction in the production costs and attention has focused again on the development of machinable mica based glass-ceramics for restorative dentistry. A crown made from glass-ceramics is shown in figure 1.

Mica glass ceramics are formed by melting and crystallising magnesium fluoro-alumino-silicate glasses. The final product is typically a multiphase solid with a highly interlocked array of 2-dimensional (sheet-like) fluormica crystals embedded in a glassy matrix. Preferential cleavage along the crystal-glass interface or the (001) basal plane of the fluormica crystal prevents macroscopic fracture of these materials during continuous machining. The machinability of the material is determined primarily by its microstructure, and consequently the development of a microstructure with interlocking mica crystals of suitable volume fraction, size and aspect ratio is of great importance. In order to produce a glass with an appropriate microstructure the nucleation and crystallisation processes must be carefully controlled. As a result much work has been carried out to characterise the production route and to optimise the properties of the final product. However, these studies have been carried out either using differential thermal analysis or by collecting X-ray diffraction patterns from material quenched from strategic temperatures during the processing route. Despite this work several questions regarding the details of phase formation during the heat treatment remain unanswered. For example, it is been reported by some workers that in similar glass ceramics the formation of fluormica occurs via the formation of precursor phases (typically chon-

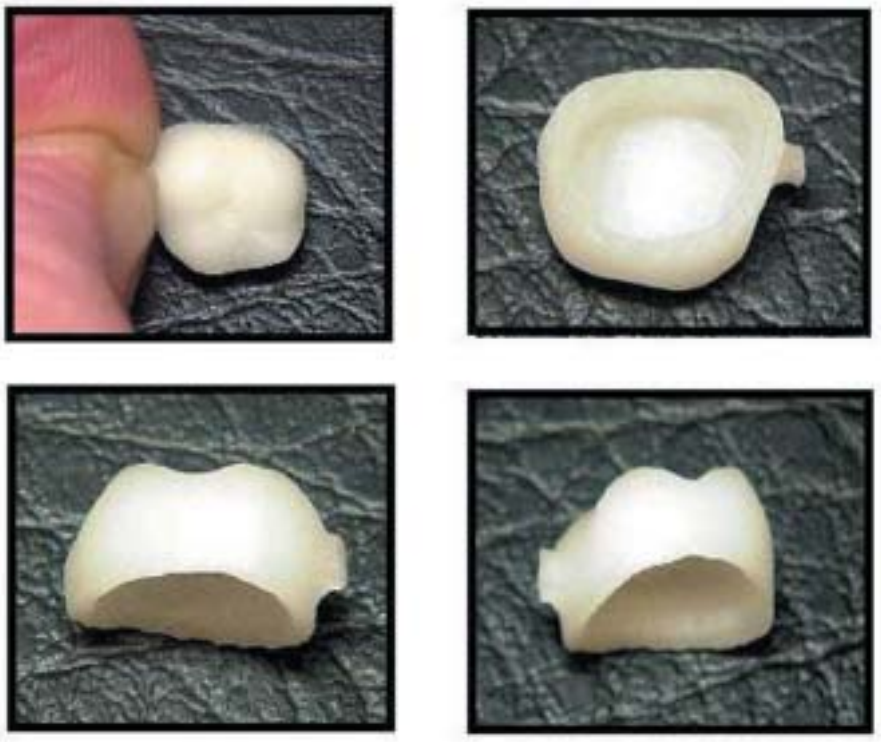

Figure 1: Examples of dental crowns produced from machinable mica glass ceramics.

Stage	Route 1	Route 2
1. Temperature ramp	10 °C/min	10 °C/min
2. Isothermal hold	644 °C, 120 min	1225 °C, 180 min
3. Temperature ramp	10 °C/min	-
4. Isothermal hold	1225 °C, 120 min	-

drodite, norbergite). Secondly, the need for low-temperature isothermal holds is unclear, as all current processing routes considered produce fluormica as the final phase.

In order to shed some light on these problems we have monitored the crystallisation of a mica based glass-ceramic with starting composition 90 mol% barium fluormica, 4 mol% cordierite, 6 mol% calcium phosphate using real time, or kinetic, neutron diffraction. We placed particular emphasis on investigating the effect of a one or two stage heat treatment on the crystallisation process. Diffraction patterns were collected every three minutes on

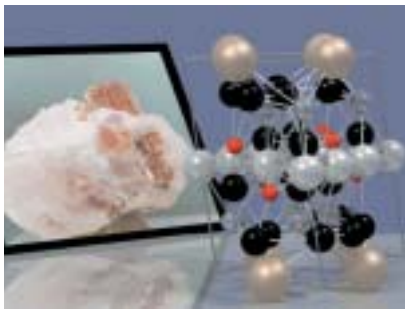

Figure 2: An image of naturally occurring fluorphlogopite crystals together with the structure of fluorphlogopite. Ba atoms are shown in gold, Mg in silver, Si/Al in grey, O in black and F in red.

D20 while heating the glass following the routes outlined in the table.

For route (1), which incorporated a nucleation hold, Bragg peaks, indicating crystallisation of the material, were first observed ~70 minutes after the start of the low temperature isothermal hold. Rietveld refinement of the data showed that these peaks arise from an orthorhombic phase which we have identified as the two layer orthorhombic, or *2Or*, mica polytype [2]. After holding at this temperature for 2 hours the sample was heated steadily to 1225 °C. At 845 °C the orthorhombic phase transformed to the more usual monoclinic (*1M*) fluormica ($Ba_{0.5}Mg_3Si_3AlO_{10}F_2$) structure shown in figure 2. Without a nucleation hold (route (2)) crystallisation of the glass is significantly delayed and does not occur until 845 °C. At this temperature the glass crystallises immediately into the monoclinic (*1M*) fluormica phase, apparently without passing through the orthorhombic mica phase.

The diffraction patterns obtained at room temperature from the final phases of routes 1 and 2 are shown in figure 3. As expected Rietveld refinement of these patterns shows that the material formed by both routes is composed predominantly of the monoclinic fluormica, (space group *C2/m* with a=5.34 Å, b=9.16 Å, c=10.05 Å and β=99.82°). The diffraction pattern obtained as the glass first crystallises is shown in figure 3(c) and is significantly different to the patterns obtained from the final phase. Rietveld refinement shows this to be an orthorhombic phase space group *Ccmm* with a=5.30 Å, b=8.96 Å, c=19.72 Å.

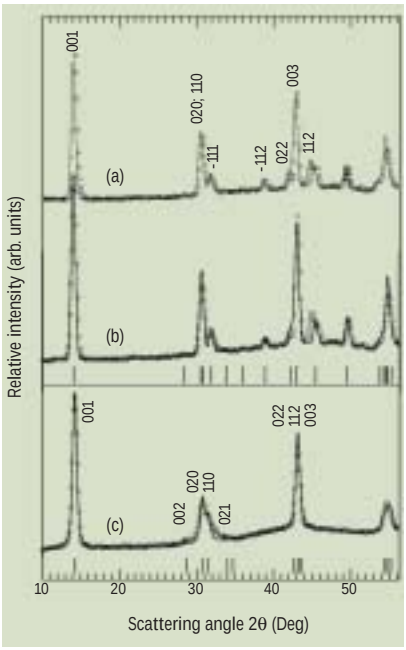

Figure 3: Diffraction patterns from final phases formed by (a) route (2) and (b) route (1). The open circles are the data and the solid lines the fit as described in the text. The diffraction pattern collected from the orthorhombic phase observed during route (1) is shown in (c).

Our measurements have proved, unambiguously, that in this series, (90 mol% barium fluormica, 4 mol% cordierite, 6 mol% calcium phosphate) precursor phases are not formed prior to the crystallisation of fluormica. It is possible, therefore, that the chondrodite and norbergite phases observed by other workers are not intrinsic to the crystallisation process but are created during the quenching process. In addition, we have shown, for the first time, that the effect of a low temperature isothermal hold is to nucleate fluormica crystals, not into the normal *1M* mica structure, but into the rather more unusual *2Or* mica polytype.

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References: [1] G.H. Beal, Reviews of Solid State Science, 3 (1989) 333
[2] Reviews in Mineralogy, Vol 13 ISBN 0-939950-17-0
[3] A. Pabst, Am Min, 40 (1955) 967