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Machinable mica-based glass-ceramic

V. SARASWATI, SARALA RAOOT
Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad 500 258, India

A glass-ceramic in the K_2O–MgO–Al_2O_3–MgF_2–SiO_2 system was prepared through the sol–gel and alkaline precipitation routes. The powders were hot pressed into workable discs. The glass-ceramic was found to be machinable with conventional tools. Its physical and mechanical properties compare favourably with commercial macor. A dependence of flexure strength on microstructure is also indicated.

1. Introduction

A machinable glass-ceramic is advantageous in producing components to a tight tolerance. Apart from being machinable, mica-based glass-ceramics are resistant to thermal shock and have good dielectric properties. The mica phase is conventionally grown, internally, by controlled heat treatment of a melted glass in the K_2O–MgO–Al_2O_3–MgF_2–SiO_2 system [1]. Recently glasses prepared through a sol–gel route are found to have higher homogeneity, better purity and lower stoichiometric losses [2]. Homogeneity is necessary for machinable glass-ceramics because an interlocked, randomly oriented uniform microstructure of mica crystallites is responsible for machinability and good strength [3]. Earlier, Hamasaki *et al.* [4] reported the sol–gel processing of a mica glass-ceramic. We present here gelation as well as alkaline precipitation routes for powder processing. The powder was hot pressed to obtain a workable disc. The physical and mechanical properties of this glass-ceramic are reported here.

2. Experimental procedure

2.1. Material preparation

The hydrolysis, polymerization and condensation of alkoxide compounds lead to the formation of gel under appropriate processing conditions. The dehydrated gel is an amorphous material and crystallizes on heating. The batch compositions for oxides are shown in Table I. The chemicals used were aluminium iso-propoxide, silicon tetra-ethoxide magnesium acetate, potassium carbonate, magnesium or ammonium fluoride. These were dissolved in their respective solvents. The pH of the sol, the order in which the solutions were mixed, the duration and temperature of refluxing were some of the parameters which affected gelation. A homogeneous, transparent or translucent gel was obtained depending upon ageing and the temperature of gelation.

Because processing influenced the evolution of crystalline phases, the following variations were made after mixing solutions of appropriate stoichiometry for batches A, B, C and D. An acidic solution of A was refluxed for 2 h resulting in a clear sol. A transparent gel formed on dehydration at 70 °C. Solution B was refluxed and gelated similar to A. Batch C was neutralized and made alkaline (pH > 8) after obtaining a clear sol. Insoluble silicate settled at the bottom, which was dehydrated along with the supernatant liquid. Composition D was precipitated similar to C, but the supernatant clear solution was decanted and the precipitate was washed and dehydrated.

The dehydrated powders were heat treated at 250, 700 and 1000 °C. The temperatures were based on prior differential thermal analysis (DTA) measurements for optimum dehydration, nucleation and growth of phlogopite crystallites [5], respectively. The powders were cold pressed before heating and the sintered compacts were characterized for physical and mechanical properties. Powders of compositions B and C calcined at 700 °C were uniaxially hot pressed into discs of 6 cm diameter. B was hot pressed at 1050 °C for 1 h at a pressure of 22 MPa and C at 950 °C for 2 h at a pressure of about 20 MPa.

2.2. Characterization methods

The densities of the pellets and hot-pressed discs were measured by the displacement method. X-ray powder diffraction technique with CuK_α radiation was adopted to identify the crystalline phases. Scanning electron microscopy with energy dispersive analysis was used for microstructure study of the fractured surface.

The hot-pressed discs of B and C were cut into long (35 mm) rectangular bars for three-point bend tests. They were polished marginally. Flexure strength values shown in Table II are an average for five bars. Smaller pieces were polished with ceria and diamond paste for Knoop hardness tests.

Thermal expansion of 3 cm long rectangular pieces were measured in a dilatometer in the temperature range 20–800 °C. Particle sizes of powder stock from drilled pieces of hot-pressed discs were determined using a Malvern particle size analyser.

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3. Results and discussion

The crystalline phases identified for heat-treated compositions A, B, C and D are shown in Table III. The influence of processing, e.g. pH of sol, is demonstrated in the results. On heating the gel powder at 250 °C, double chloride $NH_4MgCl_3 \cdot 6H_2O$ formed in A and B, when prepared under acidic conditions, whereas ammonium chloride crystallized out in C prepared under alkaline conditions. Because washing with water eliminates ammonium salts, the chloride was not present in D heated at 250 °C. The salts could also be removed by heating above 700 °C because they decomposed. The crystalline phases, which evolve in A, B, C and D after heat treatment at 700 °C are shown in Table III and the diffractograms are compared in Fig. 1. A more symmetrical form of chondrodite (as mentioned by Beall [1]) and phlogopite (trisilicic mica), were indicated in A, B and C. Phlogopite peaks were broad except for sharp lines at $d = 0.315$ nm [6]. The broad diffuse lines were similar to that observed in hydrothermally prepared phlogopite in which the X-reflections were diffuse but ordered on heating [7]. The glassy state was retained up to 700 °C in D in which magnesium fluoride separated out at 250 °C. Forsterite crystallized in D on heating above 1000 °C.

It has been reported that in the glass melt MgF_2, phase separation was found to be conducive to the growth of phlogopite crystals because it has a compatible structure [8]. This does not appear to be so on comparing the evolution of phases from our results in A, B, C and D. The hot-pressed compositions B and C (HP-B, HP-C) had trisilicic mica as the major crystalline phase. HP-C was prepared at a lower temperature and pressure, and was more porous than HP-B. Although the crystalline phases were the same, the relative intensity of the XRD peaks were different. The porosity, which can help surface crystallization, the basic nature of C compared to B, which again can modify surface properties, or slight variation in stoichiometry, could be responsible for these differences.

TABLE I Batch compositions and process differences

	Composition (wt %)				
	A	B	C	D	Macor
SiO_2	47.2	45.7	46.06	49.5	46
K_2O	10.25	10.56	8.94	4.5	10
MgO	16.57	17	26.29	21	17
Al_2O_3	19.15	19.7	11.04	16.5	16
F	6.75	6.95	7.68	8.5	4
Process difference					
pH	acidic	acidic	alkaline	alkaline, clear solution decanted and precipitate washed	

TABLE II Comparison of hot-pressed B and C with macor

	HP-C	HP-B	Macor
Density ($g\,cm^{-3}$)	2.53	2.71	2.52
Crystalline phase	trisilicic phlog.	trisilicic phlog.	trisilicic phlog.
Microhardness ($kg\,mm^{-2}$)	porosity high	236 ± 20	250
Flexure strength (MPa)	40 ± 2	71 ± 6	102
Thermal expansion ($10^{-7}\,°C^{-1}$)	107 ± 3	164 ± 4	94
Microstructure	particles needles	flakes	needles
Particle size (μm)	9, 50	4, 9, 50	

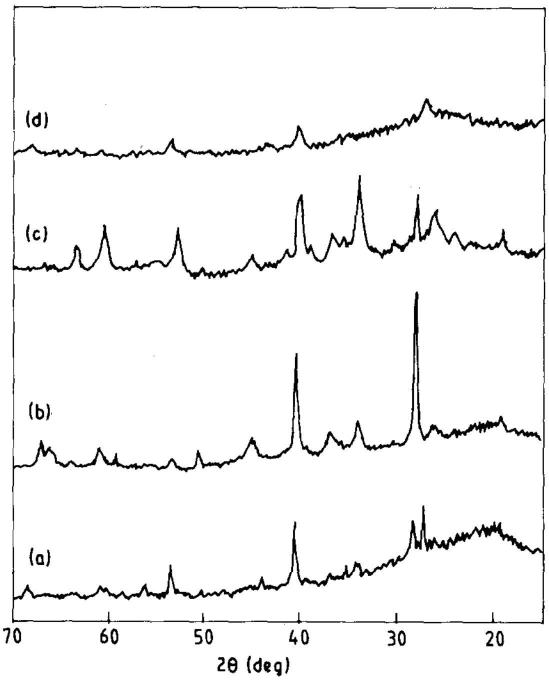

Figure 1 XRD of (a) A, (b) B, (c) C, and (d) D powders calcined at 700 °C.

TABLE III Evolution of crystalline phases with heat treatment

Composition	Heat-treatment temperature and duration		
	250 °C/6 h	700 °C/5 h	1000 °C/4 h
A	$NH_4MgCl_3 \cdot 6H_2O$	Chon., phlog., MgF_2,	Phlog.
B	$NH_4MgCl_3 \cdot 6H_2O$	Chon., phlog.	Phlog.
C	NH_4Cl	Phlog., chon.	Phlog.
D	MgF_2	MgF_2	Forsterite

The FTIR spectrum of B, C and macor were similar and show that absorption arises mainly from SiO_4 units. The 1440 cm^{-1} absorption in macor is due to B–O stretching and was absent in our compositions because no boric acid was added (Fig. 2).

The micrographs in Fig. 3 were taken of the fractured surfaces. The normally sintered pellets of B and C showed that crystallites were few in number compared to the submicrometre particulates. The diffuse and broad peaks for some reflections in Fig. 1 arise because of small thickness (micrometre or less) of plate-like crystallites (Fig. 3a). Fig. 3b shows interlocked crystallites of phlogopite in hot-pressed B. In comparison, hot-pressed C has fewer crystallites (but with larger aspect ratio) and more particulates of submicrometre size. Owing to this inhomogeneity in microstructure, flexure strength could be low (shown in Table II). Furthermore, C has a lower density compared to B, which apart from inadequate sintering is due to a lower volume fraction of crystallites. Thus for a good flexure strength, control of microstructure is indicated.

The microhardness of HP-B is 236 kg mm^{-2}, which compares favourably with macor. There was no variation in hardness with loads of 100–200 g, but was higher for loads less than 50 g. Sample C could not be polished well, because its density was low and particles were coarse.

The machinability in these glass-ceramics arises due to the cleavable nature of mica crystallites, which also deflect propagating cracks along the glass/crystal interface. A crack is blunted or localized within an interlocked crystal area and fracture propagation removes granules when a machining force is applied. Hence the powder stock removed after drilling or sawing should be related to the microstructure. When the crystallite size is small and the interlocking good, machining resolution is fine. A conventional drill machine and an ordinary hacksaw blade could drill and saw samples B and C. The chipped powder stock in B showed particle size distribution peaks around 4.7, 9.8 and 50 μm, for 8.6%, 18.5% and 32% particles. The micrographs in Fig. 3 show crystallite sizes averaging around 4 μm in hot-pressed B. The other sizes could refer to the interlocked matrix area. In C, particle sizes were widely distributed around 50 μm.

Thermal expansion measurements showed no change or hysteresis on cooling in the temperature range 20–800 °C. A repeat run followed the same pattern indicating the usability of material at least up to 800 °C. Thermal expansion values are higher compared to macor. This is due to the larger volume fraction of crystallites in B and C, compared to macor.

Physical and mechanical properties are also modified by the volume fraction of crystalline to glass phase as they have different properties and can deflect crack paths at the interfaces. Hence controlling size, growth and distribution of crystallites is essential. Microstructure is dependent on the method adopted for processing. In a gel-derived amorphous solid, the crystallization process is controlled by the presence of residual water, remnant organics, incomplete reaction and catalysts used for gelation. Comparing B and C, phlogopite phase sets in earlier in C as expected. Whether it is a solid state reaction at high temperature or a chemical reaction at low temperature, a cation would tend to have an environment with an optimum number of oxygen ions dictated by the ratio of their ionic radii and their valencies measured as a cationic field strength [9]. Above the glass transition temperature (~ 600 °C) the ionic motions are appreciable and differences in gel-derived amorphous oxide should disappear for the same composition. The lower flexure strength in HP-C could be ascribed to the pressing parameters as much as to the process. HP-B reasonably compares with macor. With a better control of glass phase or the microstructure in general, further improvement in flexure strength is possible. Because surface crystallization is likely in glasses, especially when powders are sintered, processing variations, which influence surface properties are likely to affect the microstructure and thereby mechanical properties of a glass-ceramic.

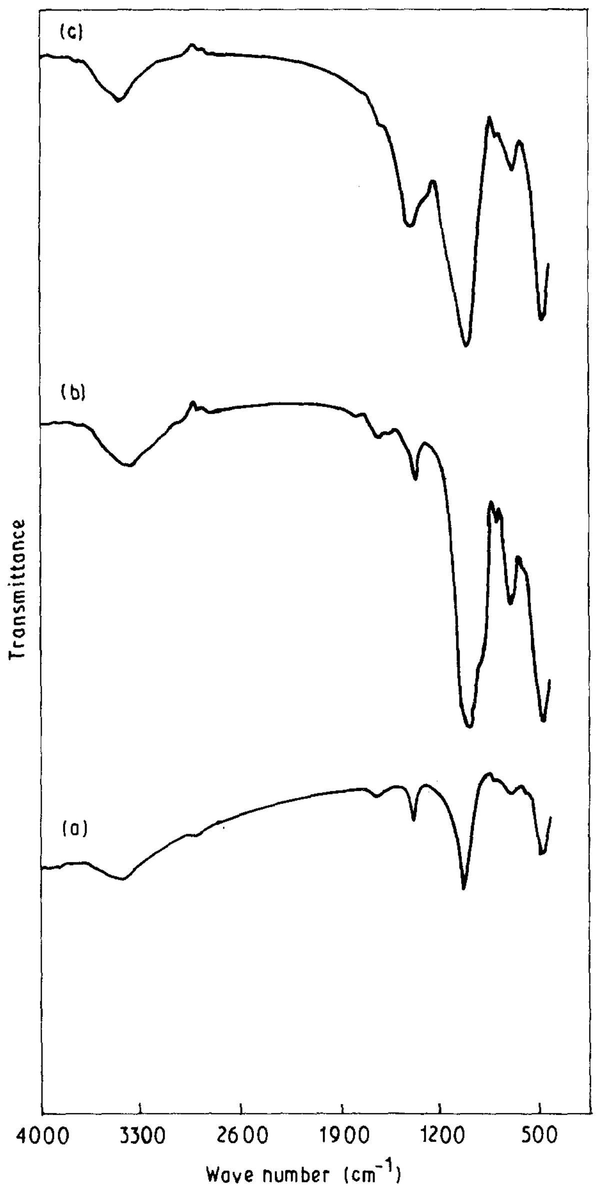

Figure 2 FTIR spectra in hot-pressed (a) B and (b) C, compared with (c) macor.

In summary, we show that workable, hot-pressed discs of machinable glass-ceramics can be prepared

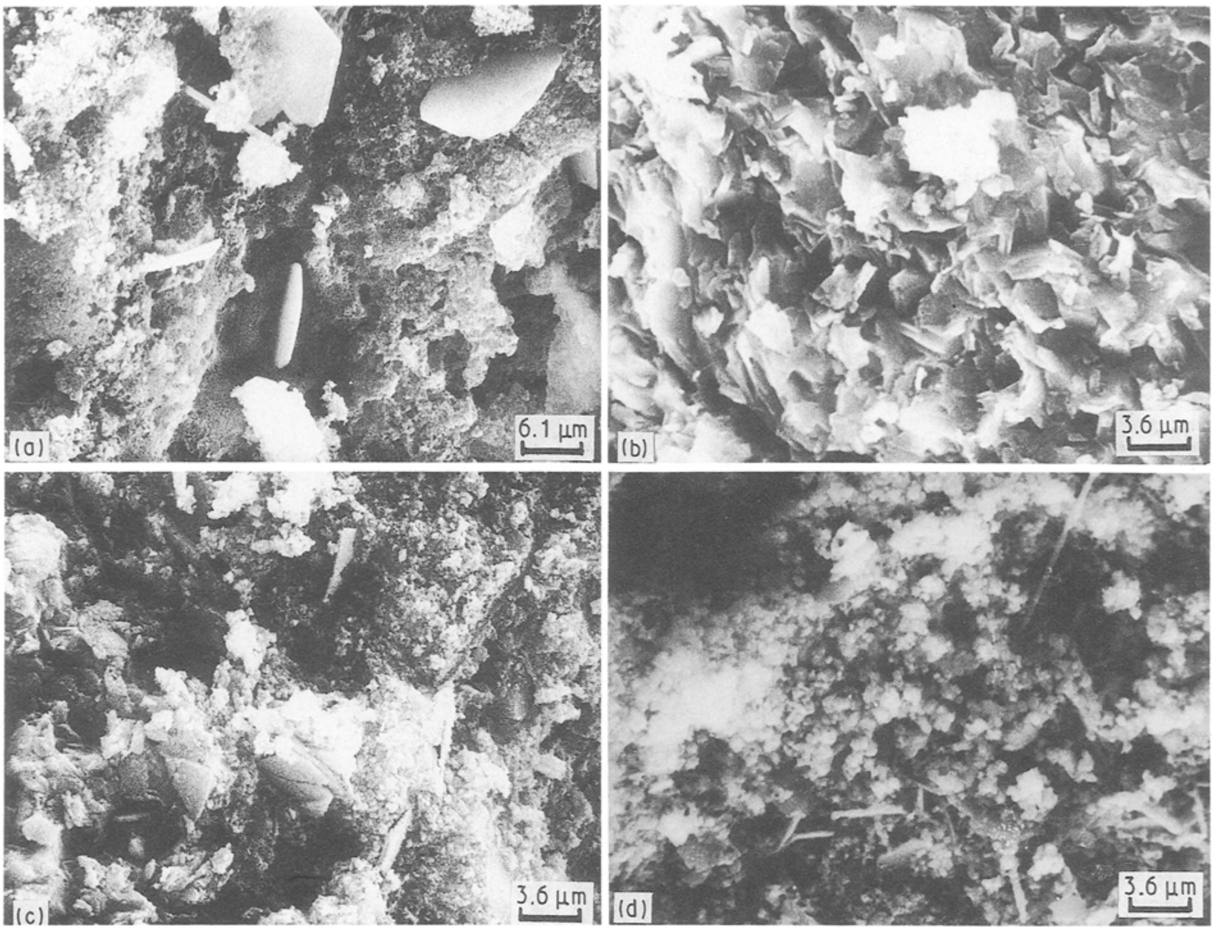

Figure 3 Micrographs of the fractured surface in samples, (a) B, sintered for 12 h at 700 °C, (b) B, hot pressed, (c) C, sintered for 12 h at 1000 °C, (d) C, hot pressed.

by the gelation as well as the alkaline precipitation routes. The strength of these glass-ceramics depends upon the microstructure, which again is controlled by the process as well as pressing conditions.

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