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Crystallization Behavior and Properties of $BaO \cdot Al_2O_3 \cdot 2SiO_2$ Glass Matrices

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CRYSTALLIZATION BEHAVIOR AND PROPERTIES OF $BaO.Al_2O_3.2SiO_2$ GLASS MATRICES

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SUMMARY

Glass of stoichiometric celsian composition, $BaO.Al_2O_3.2SiO_2$, is a potential glass-ceramic matrix for high-temperature composites. The glass has a density of 3.39 g/cm^3, thermal expansion coefficient of $6.6 \times 10^{-6}/^{o}C$, glass transition temperature of $910^{o}C$, and dilatometric softening point of $925^{o}C$. On heat treatment, only hexacelsian crystallized out on the surface, but both celsian and hexacelsian were present in the bulk. Effects of cold isostatic pressing (CIP), sintering, and hot pressing, in the presence and absence of an additive, on the formation of the celsian phase in the glass have been studied. CIPed samples, after appropriate heat treatments, always crystallized out as celsian whereas the presence of 5 - 10 weight % of an additive was necessary for formation of celsian in sintered as well as hot pressed specimens. Green density increased with CIPing pressure but had no effect on sintered density. Hot pressing resulted in fully dense samples.

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INTRODUCTION

Because of the high melting point (1760°C) of celsian, its oxidation resistance, low thermal expansion coefficient (2.29 x 10^{-6}/°C from 20 - 1000°C), and phase stability[1] up to ~1590°C, glass of stoichiometric $BaO.Al_2O_3.2SiO_2$ composition is being investigated as a precursor matrix material for fabrication of fiber-reinforced, glass-ceramic composites at NASA Lewis. These composites are possible candidates as high-temperature structural materials for high-efficiency, high-performance engines in aerospace propulsion and power systems of the future.

Hexacelsian always crystallizes out first on thermal treatment of the $BaO.Al_2O_3.2SiO_2$ glass. Hexacelsian is the high temperature polymorph and is metastable below ~1590°C. It has a high thermal expansion coefficient (8.0 x 10^{-6}/°C from 300 - 1000°C) and, moreover, at ~300°C undergoes[2] a rapid, reversible displacive transformation into the orthorhombic form accompanied by a large volume contraction (~3%) and is thus unsuitable as a structural material and composite matrix. Monoclinic celsian is thermodynamically stable below ~1590°C and is the desired phase for structural applications. Unfortunately, the transformation of hexacelsian into celsian is very sluggish. For successful use of this glass-ceramic as a matrix material, it is necessary to manipulate the processing methods for direct precipitation of celsian in the glass.

The objectives of the present work were to measure the physical properties of the $BaO.Al_2O_3.2SiO_2$ glass composition (referred to as BAS-C), study its crystallization behavior, and optimize the processing conditions for direct crystallization of celsian in the glass matrix. Effects of cold isostatic pressing, sintering, hot pressing and the presence of an additive on formation of the celsian phase have been investigated. Crystallization studies of two related glass compositions in the barium aluminosilicate system were recently reported[3,4] by the present workers.

EXPERIMENTAL METHODS

Glass Melting

Glass of stoichiometric celsian composition $BaO.Al_2O_3.2SiO_2$ was melted at ~2000 - 2100°C in a continuous electric melter with Mo electrodes using laboratory grade $BaCO_3$, Al_2O_3, and SiO_2. A well-blended stoichiometric mixture of the starting materials was continuously fed into the furnace. The molten glass was continuously withdrawn through a manually controlled needle valve, and quickly quenched resulting in homogeneous, clear, and colorless flakes or rods of glass. The flakes were wet ground in an attrition mill using zirconia or alumina media, which resulted in fine glass powder having an average particle size of <2.5 μm.

Chemical Analysis

The Ba, Al, and Si contents in the glass were determined from wet chemical analysis and Mo by x-ray fluorescence technique.

The estimated accuracy of the two methods was ±1.0% and ±10%, respectively. The analyzed glass composition in weight % was determined to be BaO:39.5, Al_2O_3:28.7, SiO_2:31.3, and MoO_3:0.015 as compared with the batch values of BaO:40.9, Al_2O_3:27.1, SiO_2:32.0, and MoO_3:0.0 . The presence of Mo is probably due to the Mo electrodes used in the electric melting of the glass. A slight loss of silica is not unexpected.

Heat Treatment

Heat treatments were carried out in air using a programmable Lindberg box furnace with temperature control better than ±5°C of the set value. Glass flakes were nucleated for 1h at 850, 900, or 950°C followed by further heat treatment at 1080, 1150, 1220, or 1290°C for 4h and furnace cooled.

Hot Pressing

Glass powder, with and without 5 weight % of an additive, was hot pressed into rectangular samples in a graphite die at various temperatures between 1200 to 1400°C for 2h under a pressure of 24 MPa in vacuum. After hot pressing the samples were slow cooled. Grafoil was used to prevent any reaction between the sample and the die.

Cold Isostatic Pressing (CIP) and Sintering

Glass powder, with and without 5 weight % of an additive, was cold pressed into ~ 7.9 x 5.5 x 55 mm rectangular bars, CIPed at ~414 MPa, and sintered at various temperatures between 1200 to

1500°C for 20h in air. Cold pressed bars were also CIPed at various pressures between 69 to 414 MPa and sintered at 1300°C for 20h in air.

Density

Densities of the hot pressed and sintered specimens were measured by the immersion method using water.

Thermal Expansion Coefficient

Linear thermal expansion coefficient (α) and softening point (T_s) of the glass were measured in static air on a glass rod about 2.5 cm long using an Orton automated recording dilatometer at a heating rate of 3°C/min.

Flexural Strength

The flexural strength of the sintered bars was measured in 3-point bending using an Instron machine. The span length of the test samples was ~3.2 cm. All tests were run at a cross head speed of 0.127 cm/min.

Differential Scanning Calorimetry (DSC)

Glass transition (T_g) and crystallization (T_x) temperatures of the glass were determined from DSC performed on bulk and powder samples using a Stanton-Redcraft DSC 1500 system which was interfaced with a computer data acquisition and analysis system. About 35 - 50 mg of the glass sample was contained in a platinum DSC pan and scanned from ambient temperature to ~1450°C at a heating rate of 40°C/min. Dry argon or nitrogen flowed through the DSC cavity during the measurements.

X-ray Diffraction (XRD)

Crystalline phases present in the heat treated glass samples were identified from powder XRD patterns recorded at room temperature using a step scan procedure ($0.03^{o}/2\theta$ step, count time 0.4s) on a Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing copper K_{α} radiation.

Microscopy

Heat treated glass flakes were mounted in an epoxy, grind, and polished to a 0.5 μm finish. The polished specimens were lightly etched by immersing in an etching solution (1ml conc. HCl + 1ml 48% HF + 100ml distilled H_2O) for 5 to 10s. Microstructures of the etched specimens were observed in an optical microscope as well as in a JEOL JSM-840A scanning electron microscope (SEM). A thin layer of gold was deposited onto the sample surface before viewing in the SEM.

RESULTS AND DISCUSSION

The glass properties -- density, thermal expansion coefficient, glass transition temperature, T_g, and dilatometric softening point, T_s, -- are given in Table 1. The BAS-C glass is extremely refractory for silicate glasses with a dilatometric softening point of $925^{o}C$. However, for high temperature composite applications it is necessary to crystallize the glass to the much refractory celsian, $T_m = 1760^{o}C$.

DSC scans for the powdered and bulk glass are given in Figure 1. The enthalpy of crystallization, ΔH, for the powdered sample

was determined to be -211 J/g at 1098°C for the crystallization of hexacelsian. The crystallization exothermic peak was sharper and occurred at a lower temperature for the powder sample than for the bulk glass. For the bulk glass the crystallization enthalpy was -163 J/g at 1272°C. The broader peak at a higher temperature would be consistent with surface nucleation on the glass flake. The lower ΔH for the bulk may have been due to incomplete crystallization of the glass or due to different enthalpies for the crystallization of the celsian and hexacelsian phases.

Nucleation and crystal growth heat treatments used for the bulk glass are given in Table 2. Under all conditions both hexacelsian and celsian were crystallized even though the thermodynamically stable phase is celsian. The glassy phase was indicated by a broad peak in the XRD pattern. All of the samples were white and opaque in appearance after heat treatment. As reported earlier by Bahat[5], the complete crystallization of celsian is very difficult and under some temperature conditions may never be achieved. Over the optimal nucleation range of 850 - 950°C with growth at temperatures from 1080 - 1290°C, incomplete crystallization of hexacelsian was obtained. This was the major phase present with minor amounts of celsian.

Figure 2 provides the XRD evidence for surface crystallization in these glasses. Only hexacelsian was detected by XRD on the surface of the heat treated flakes, but when the material was ground, both celsian and hexacelsian were found to

be present. This nucleation was presumably heterogeneous, but the mechanism and conditions for the nucleation of the celsian in the interior of the flake have not been determined. Based upon these results, it would seem that once the metastable hexacelsian phase has formed it is an extremely sluggish transformation to the stable celsian phase.

The effect of an additive is shown in Figure 3. With 5 and 10 wt% concentration of the additive, under different heat treatment conditions, the celsian phase was formed in the glass powders. Without the additive both hexacelsian and celsian were formed; however, it was possible to nucleate the celsian phase directly.

Similar results were obtained with hot pressing with nucleation at a higher temperature and growth at a lower temperature as shown in Figure 4. In the absence of the additive, a mixture of hexacelsian and celsian was formed, whereas only celsian was formed in the absence of the additive.

The results of cold pressing, CIPing at ~414 MPa and sintering at various temperatures with and without the additive are shown in Table 3. With CIPing, celsian was formed under all conditions studied for sintering in air for 20 h at temperatures from 1200 - 1500^{o}C. The density and bend strength did not vary significantly under these conditions. In Table 4 the effect of varying the CIPing pressure from 0 to 414 MPa is shown. All samples were sintered at 1300^{o}C for 20h in air. The green density increased with CIPing pressure, as expected, but there was no effect on the sintered density. The low densities were due to

incomplete consolidation of the samples and not due to the presence of hexacelsian. Increasing the CIPing pressure did not affect the phase formation. For both sets of samples, with and without the additive, the measured bend strengths were in the 62 to 124 MPa range base on a single sample under each condition. The reason for direct crystallization of celsian in CIPed samples is not clear at this time.

For hot pressed tapes a mixture of celsian and hexacelsian was formed at temperatures from 1200 - 1400^{o}C at a pressure of 24 MPa for 2h. The complete data are given in Table 5. With the additive, only celsian was formed at temperatures above 1200^{o}C. The hot pressed density was close to the theoretical value. The presence of the additive was necessary for complete crystallization of celsian. Without it a mixture of celsian and hexacelsian crystallized similar to the nucleation and growth study results in bulk glass. The amount of hexacelsian formed in the samples without the additive was not large as can be seen from XRD results and by comparing the hot pressed densities with the density of celsian.

Optical and SEM micrographs of BAS-C glass heat treated under various conditions are shown in Figures 5 - 7. In Figure 5 the large grained crystals at the surface are hexacelsian while the finer grained crystals in the interior are believed to be celsian. The optical and SEM micrographs confirmed the distribution of hexacelsian and celsian crystals in the heat treated bulk samples as determined by the XRD results.

SUMMARY OF RESULTS

Under various nucleation and crystal growth conditions a mixture of hexacelsian and celsian always crystallized from a stoichiometric celsian glass, BAS-C. Hexacelsian crystallized on the surface, and both celsian and hexacelsian crystallized in the bulk. The presence of 5 or 10 wt% of an additive was necessary for the crystallization of only celsian in sintered and hot pressed powders. CIPed samples of the glass powder always crystallized as celsian under the conditions of temperature and pressure investigated. Increasing the CIPing pressure increased the green density but had no effect on the sintered density. Hot pressed samples were fully dense and crystallized to celsian in the presence of the additive. Under the processing conditions investigated there appeared to be no change in bend strengths.

CONCLUSIONS

Crystallization of celsian from the $BaO.Al_2O_3.2SiO_2$ glass composition is feasible under appropriate heat treatments after cold isostatic pressing or in the presence of 5 - 10 weight % of an additive.

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TABLE 1. PROPERTIES OF BAS-C GLASS

Density,	3.390 ± 0.004 g/cm^3
Thermal Expansion Coefficient, α	$6.6 \times 10^{-6}/^{\circ}C$ (25-800°C)
Glass Transition Temperature, T_g	$910 \pm 2^{\circ}C$
Dilatometric Softening Point, T_s	$925^{\circ}C$

TABLE 2. CRYSTALLINE PHASES PRESENT IN BAS-C GLASS AFTER NUCLEATION AND CRYSTAL GROWTH AT VARIOUS TEMPERATURES

Heat Treatment		Crystal Phases*
Nucleation Temperature °C (1h)	Growth Temperature °C (4h)	
850	1080	HC(M), C(m), g
	1150	HC(M), C(m), g
	1220	HC(M), C(m), g
	1290	HC(M), C(m)
900	1080	HC(M), C(m), g
	1150	HC(M), C(m), g
	1220	HC(M), C(m), g
	1290	C(M), HC(m), g
950	1080	HC(M), C(m), g
	1150	HC(M), C(m)
	1220	HC(M), C(m)
	1290	HC(M), C(m), g

All samples were white and opaque in appearance.
* HC - Hexacelsian, C - Celsian, g - glass
(M) - Major phase, (m) - minor phase

TABLE 3. PROPERTIES OF BAS-C GLASS WITH AND WITHOUT ADDITIVE COLD PRESSED, CIPED AT 414 MPa AND SINTERED AT VARIOUS TEMPERATURES FOR 20h IN AIR

Sintering Temperature (^{o}C)	Additive (wt%)	Density (g/cm^3)	Bend Strength (MPa)
1200	0	3.06	124
1300	0	3.00	117
1400	0	2.87	62
1500	0	2.91	69
1200	5	3.05	103
1300	5	2.98	83
1400	5	2.86	83
1500	5	2.89	83

All samples crystallized as celsian

TABLE 4. PROPERTIES OF BAS-C GLASS POWDER COLD PRESSED, CIPED AT VARIOUS PRESSURES AND SINTERED AT 1300°C FOR 20h IN AIR

CIPing Pressure (MPa)	Green Density (g/cm^3)	Sintered Density (g/cm^3)	Bend Strength (MPa)
0	-	3.04	83
69	1.83	3.03	69
138	1.86	3.02	69
207	1.96	3.00	69
276	1.99	3.00	76
345	2.13	3.04	69
414	2.13	3.05	90

All samples crystallized as celsian.

TABLE 5. PROPERTIES OF BAS-C GLASS POWDER HOT PRESSED AT VARIOUS TEMPERATURES AT 24 MPa FOR 2h IN VACUUM

Hot Pressing Temperature (^{o}C)	Additive (wt%)	Density (g/cm^3)	Crystalline Phases* From XRD
1200	0	3.32	C(M), HC(m)
1300	0	3.34	C(M) > HC(M)
1400	0	3.39	C(M), HC(m)
1400 / 1200	0	3.36	C(M), HC(m)
1400 / 1300	0	3.36	C(M), HC(trace)
1200	5	3.38	C(M), HC(m)
1300	5	3.38	C
1400	5	3.41	C
1400 / 1200	5	3.38	C

*C - Celsian, HC - Hexacelsian
(M) - Major Phase, (m) - Minor Phase
Theoretical Density of $BaAl_2Si_2O_8$:
Celsian = 3.390 g/cm^3, Hexacelsian = 3.296 g/cm^3

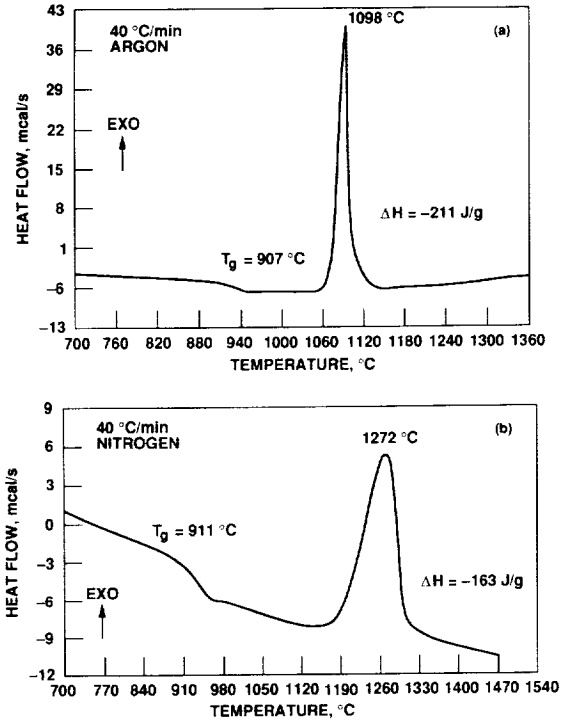


Figure 1. - DSC scans of BAS-C glass (a) powder and (b) bulk samples recorded at a heating rate of 40 °C/min.

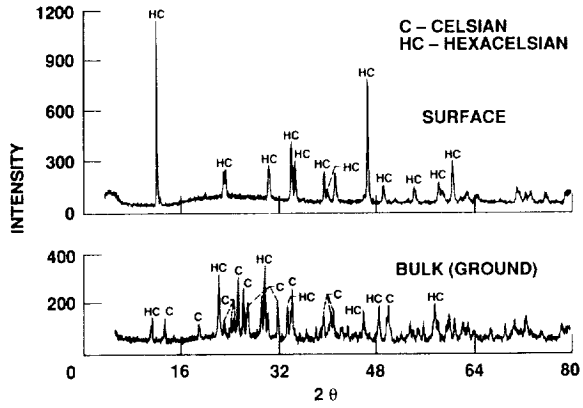


Figure 2. - XRD patterns from surface and bulk BAS-C glass flake heat treated at 900 °C, 1 h and 1290 °C, 4 h.

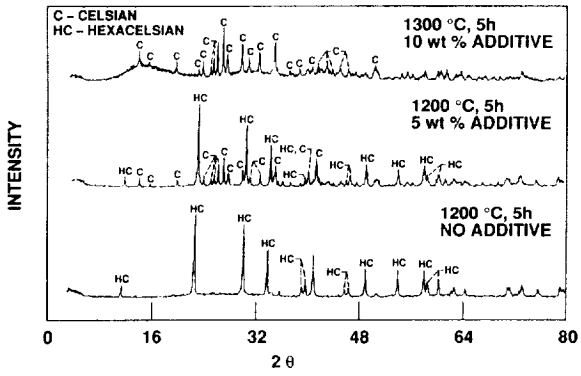


Figure 3. - XRD patterns of heat treated BAS-C glass powders with and without an additive.

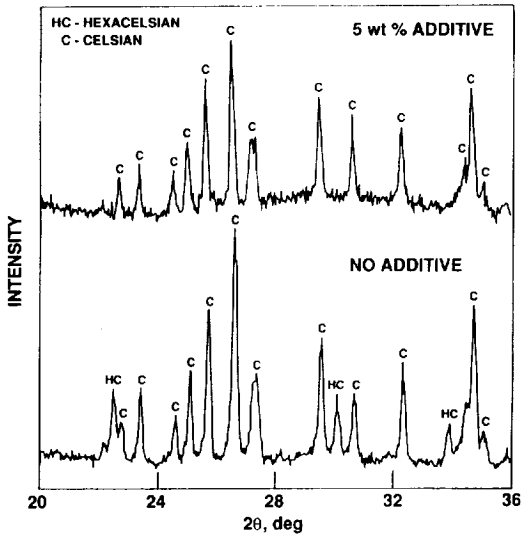


Figure 4. - Powder XRD patterns of BAS-C glass with and without additive hot pressed at 1400 °C, 2 h and 1200 °C, 2 h.

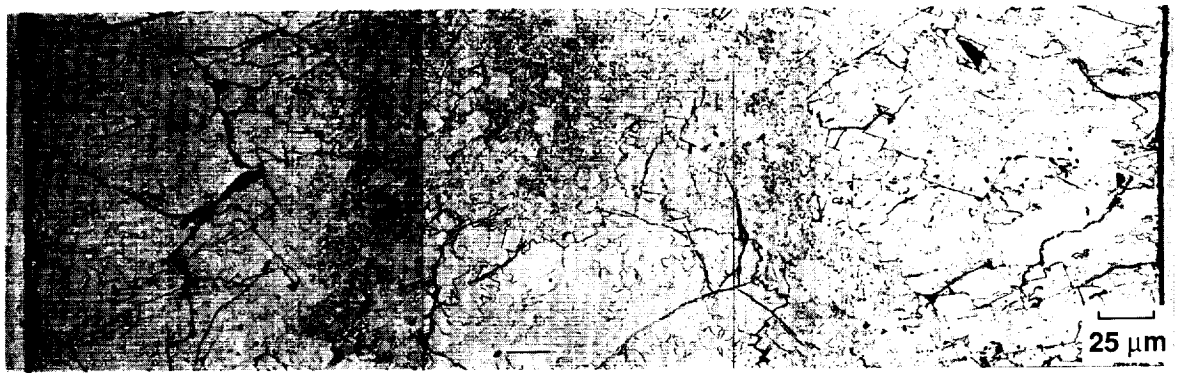
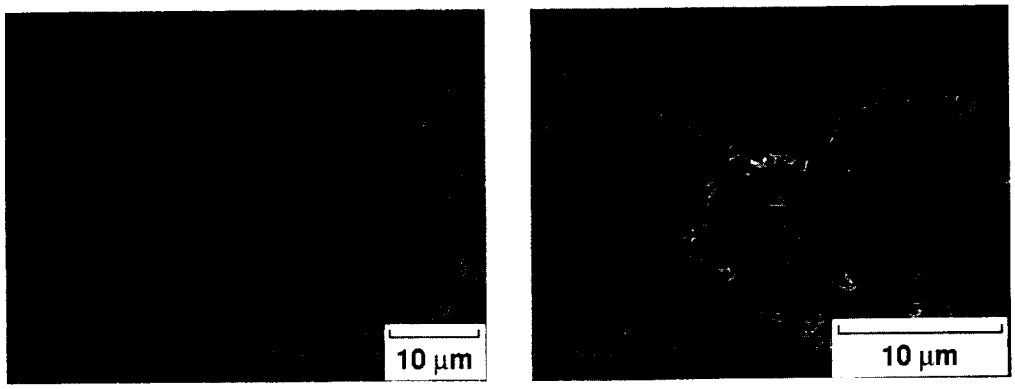
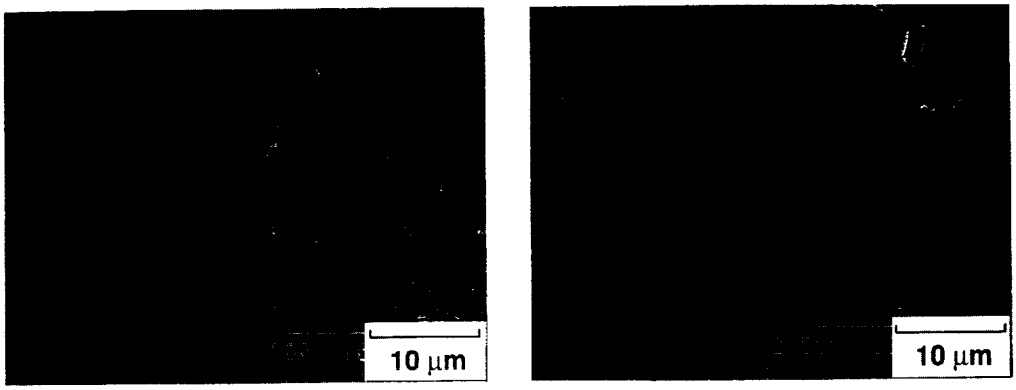


Figure 5. - Optical micrograph of BAS-C glass flake heat treated at 900 °C for 1 h and 1290 °C for 4 h, polished and etched (sample edges are visible on the right and left sides of the micrograph).



(a) 850 °C, 1 h + 1290 °C, 4 h



(b) 900 °C, 1 h + 1290 °C, 4 h

Figure 6. - SEM micrographs of BAS-C glass flakes heat treated under different conditions, polished and etched.

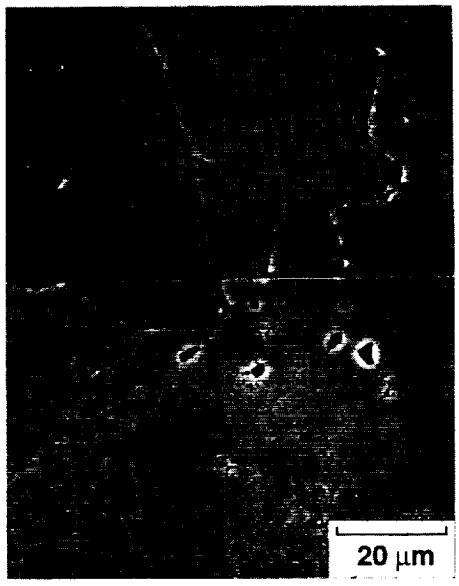


Figure 7. - SEM micrograph of BAS-C glass flake heat treated at 900 °C for 1 h and 1290 °C for 4 h, polished and etched.

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16. Abstract

Glass of stoichiometric celsian composition, $BaO \cdot Al_2O_3 \cdot 2SiO_2$, is a potential glass-ceramic matrix for high-temperature composites. The glass has a density of 3.39 g/cm^3, thermal expansion coefficient of 6.6×10^{-6}/°C, glass transition temperature of 910 °C, and dilatometric softening point of 925 °C. On heat treatment, only hexacelsian crystallized out on the surface, but both celsian and hexacelsian were present in the bulk. Effects of cold isostatic pressing (CIP), sintering, and hot pressing, in the presence and absence of an additive, on the formation of the celsian phase in the glass have been studied. CIPed samples, after appropriate heat treatments, always crystallized out as celsian whereas the presence of 5-10 weight % of an additive was necessary for formation of celsian in sintered as well as hot pressed specimens. Green density increased with CIPing pressure but had no effect on sintered density. Hot pressing resulted in fully dense samples.

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