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Journal of the European Ceramic Society 23 (2003) 2203–2209
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# Synthesis of $BaAl_2Si_2O_8$ glass-ceramic by a sol-gel method and the fabrication of $SiC_{pl}/BaAl_2Si_2O_8$ composites

Feng Ye[a,*], J.C. Gu[a], Y. Zhou[a], M. Iwasa[b]

[a]*School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China*
[b]*National Institute of Advanced Industrial Science and Technology, AIST Kansai, Ikeda, Osaka 563-8577, Japan*

Received 28 July 2002; received in revised form 18 December 2002; accepted 5 January 2003

**Abstract**

$BaAl_2Si_2O_8$ glass ceramics were synthesized by sol-gel using partial alkoxides. The crystallization behavior of $BaAl_2Si_2O_8$ gel was characterized by XRD, DTA and TGA techniques. Barium aluminosilicate glass ceramic matrix composites reinforced with SiC platelets were fabricated by hot pressing method. The microstructure, mechanical properties and fracture behavior of the composites were investigated by X-ray diffraction, scanning and transimision electron microcopies, and three point bending tests. The results show that the flexural strength and the fracture toughness of the $SiC_{pl}$/BAS composites increases with increasing SiC platelet content. By incorporation of 30 vol.% $SiC_{pl}$, the flexural strength and the fracture toughness of the composites increase 80% and 114% compared to the pure BAS matrix, respectively. The main toughening mechanism is crack deflection.


*Keywords:* $BaAl_2Si_2O_8$; Composites; Mechanical properties; Platelets; SiC platelets; Sol-gel processes

## 1. Introduction

Since Barium aluminosilicate ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) (BAS) has one of the highest melting temperature (1760 °C) among the glass-ceramic materials and the monoclinic form exhibits a low thermal expansion coefficient ($2.29\times10^{-6}$/°C from 22 °C to 1000 °C),[1] BAS is attracting considerable interest for diverse applications such as structural components, electronic and matrix for ceramic-matrix composites. However, like other glass ceramics, the pure BAS ceramic matrix exhibits poor mechanical properties, and hence this limits its use in many structural applications. It is well known that the mechanical properties of glass, ceramic and glass-ceramic matrices can be improved by adding a second phase, such as whisker,[3–5] platelet[6-8] or fiber.[9] SiC whiskers have been widely used to reinforce glass-ceramics, resulting in the composites with excellent properties.[3,4,10] However platelets have been introduced into ceramic composite matrices as a potential replacement for whiskers because of the toxic nature of whiskers and the improvement in densification of the composites. On the other hand, platelets give better fracture resistance than whiskers although they may reduce the strength.

The present paper describes the fabrication, mechanical properties and microstructure of barium aluminosilicate composites reinforced with different volume fractions of SiC platelets. The procedure of BAS gel synthesis is also described.

## 2. Experimental procedure

The materials used in this study were BAS glass-ceramic composites reinforced with different volume fractions of SiC platelet (from 10 to 40 vol.%). The BAS matrix powders were synthesized through hydrolysis of alkoxides. The synthesis procedure of the BAS gels and the gel-derived glasses is demonstrated in Fig. 1. The solution of $TEOS/CH_3COOH$ was poured into the solution of aluminum isopropoxide, and then the solution of barium acetate was added under continuous stirring. The mixed solution was kept at room temperature

* Corresponding author at current address: National Institute of Advanced Industrial Science, Technology, AIST Kansai, Ikeda, Osaka 563-8577, Japan.
*E-mail address:* feng.ye@aist.go.jp (F. Ye).

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doi:10.1016/S0955-2219(03)00042-6

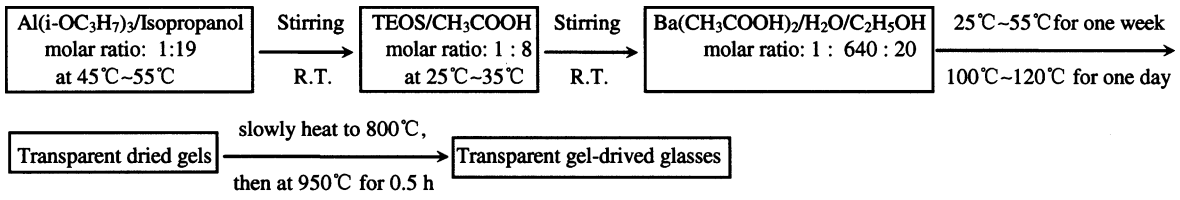


Fig. 1. Synthesis procedure of BAS gels and gel-derived glasses.

in air until gelation occurred. The gels were placed at 25∼35 °C for 1 week and then at 100∼120 °C for another day in order that the hydrolysis–polymerization reactions were conducted. The dried gels were heated to 500 °C at a heating rate of 5 °C/min, and then soaked at 800 °C for 10 h to remove the residual organics. The BAS glasses were obtained by heating the organic-free gels at 950 °C for 0.5 h.

The chemical composition of $BaAl_2Si_2O_8$ matrix powders is shown in Table 1. As shown in Table 1, 20 wt.% celsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) seeds (particle size, 2∼3 μm) were incorporated into the BAS matrix to improve the hexacelsian-to-celsian phase transformation during sintering. The seeds were obtained through the crystallization treatment of BAS glass powders with 3 wt.% $Li_2O$ additives.[2] The SiC platelets used in this study (SF grade, C-Axis technology, Canada) have a diameter of 9–24 μm and a thickness of 1–6 μm. The BAS glass-ceramic powders, BAS seeds and SiC platelets (0∼40 vol.% $SiC_{pl}$) were mechanically mixed in ethyl alcohol using $ZrO_2$ balls for 12 h. The slurries were dried and aggregates were dispersed by hand as required. The dried blends were then hot-pressed in graphite dies at 1370 °C for 30 min under a pressure of 10 MPa in a nitrogen atmosphere into disks of 55 mm diameter and 6 mm thickness. The densities of the samples were measured by Archimedes' method in distilled water at 20 °C.

The fracture toughness and the flexural strength of the composites were measured in air at room temperature. All flexural bars were machined with the tensile surface perpendicular to the hot-pressing axis direction. Flexural strength measurement were performed on bar specimens (3 mm×4 mm×36 mm) using a three-point bend fixture with a span of 30 mm. Fracture toughness measurements were performed on single-edge-notch beam specimens (SENB) with a span of 16 mm, and a half-thickness notch was made using a 0.33 mm thick diamond wafering blade. Six bars were tested for each composition.

Table 1
Chemical composition of BAS matrix powders (wt.%)

| Composition of BAS | | | BAS celsian seeds |
|---|---|---|---|
| BaO | $Al_2O_3$ | $SiO_2$ | |
| 32.72 | 21.68 | 25.60 | 20 |

The characterization of BAS gels was investigated by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) (Guinier-Hägg camera, Cu$K_{\alpha1}$ radiation, $\lambda = 1.5405981$ Å) techniques. The phases of the produced $SiC_{pl}$/BAS composites were also characterized by XRD. Fracture surface and crack propagation path produced by Vickers indenter on the composites were examined by scanning electron microscopy (SEM). The microstructures of the composites were characterized by transmission electron microscopy (TEM). Thin foil specimens taken normal to the hot-pressing axis were prepared by dimpling and subsequent ion-beam thinning.

## 3. Results and discussion

### 3.1. Crystallization of the BAS gel

The gels dried at 60 °C were investigated by DTA and TGA techniques, as shown in Fig. 2. The result of TGA shows that all the weight loss has taken place below 700 °C, above which no more significant weight loss

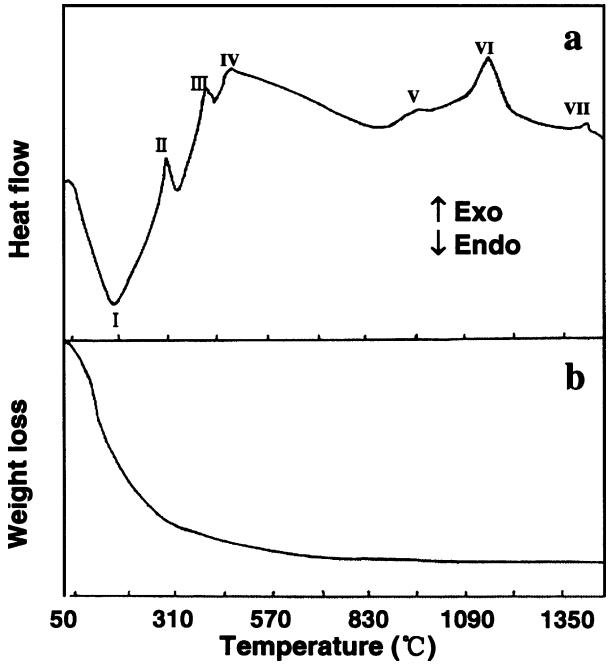


Fig. 2. DTA and TGA curves of the BAS gel dried at 60 °C: (a) DTA curve, (b) TGA curve.

occured. Many reactions occur in this process, which cause the endothemic or exothemic peaks on the DTA curve. The obvious endothemic peak (I) at 200 °C corresponds to the evaporation of water and solvents. Below 600 °C, there are three exothemic peaks (II, III, IV) due to the oxidizing pyrolysis of residual organics in the gels. The exothemic peak (V) at 941 °C is due to the transformation from gel to glass. The sharp exothemic peak (VI) at 1152 °C is due to the crystallization of hexacelsian.

The crystallization behavior of the BAS gel is shown in Fig. 3. It reveals that the gel remained amorphous up to 950 °C, above which hexacelsian started to crystallize. All gel crystallizes to hexacelsian after heat-treatment at 1100 °C for 0.5 h.

### 3.2. The effect of $Li_2O$ and seeds on the transformation of $Bal_2Si_2O_8$ gel

As shown in Fig. 3, the BAS gel always crystallizes to metastable hexagonal phase and it is very difficult for BAS to transform from hexacelsian to celsian phase due to the different solid solution of $SiO_2$.[11] However, as the matrix of composites, the celsian phase is a preferred polymorph because of its lower thermal expansion, high thermal stability and oxidation resistance.[12] It has been found that doping with additives could catalyze monoclinic celsian crystallization in glasses and gels. In this study, 3 wt.% $Li_2O$ or 20 wt.% celsian seeds were added to BAS glass powder to promote its hexacelsian →celsian transformation.

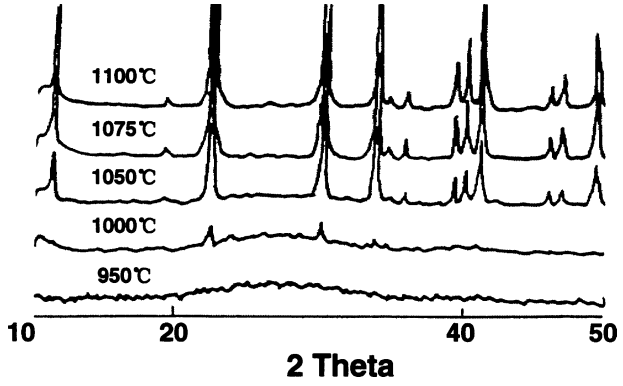


Fig. 3. Powder XRD patterns of $Ba_2Al_2Si_2O_8$ gel heated at various temperatures for 0.5 h. All the peaks are from hexacelsian phase.

The XRD result of BAS sample with 3 wt.% $Li_2O$ is shown in Fig. 4a. It reveals that 3 wt.% $Li_2O$ can effectively promote the hexacelsian→celsian transformation, and the pure celsian could be obtained after heat treatment at 1200 °C for 0.5 h. This can be explained considering that the incorporation of $Li_2O$ decreases the viscosity of liquid and hence improves the solid diffusion of $SiO_2$. It has been suggested that, by adding $Li_2O$, the formation of monoclinic celsian can be obtained while preventing hexacelsian formation.[13,14] But, the presence of $Li_2O$ will strongly affect its high-temperature mechanical properties because of the low eutectic temperature.[15] Fig. 4b shows that incorporation of 20 wt.% celsian seeds also promotes this transformation due mainly to the isostructural seeding effect. The seeding with monoclinic crystals can assist the formation of monoclinic celsian as well as hexacelsian-to-celsian phase transition through heterogeneous effect.[14] It will be very useful in realizing the hexacelsian →celsian transformation. In the next section about $SiC_{pl}$/BAS composites, 20 wt.% celsian seeds were also added to enhance the celsian formation during sintering.

### 3.3. Microstructure of $SiC_{pl}$/BAS composites

The relative densities of the $SiC_{pl}$/BAS composites are summarized in Table 2. It reveals that the density

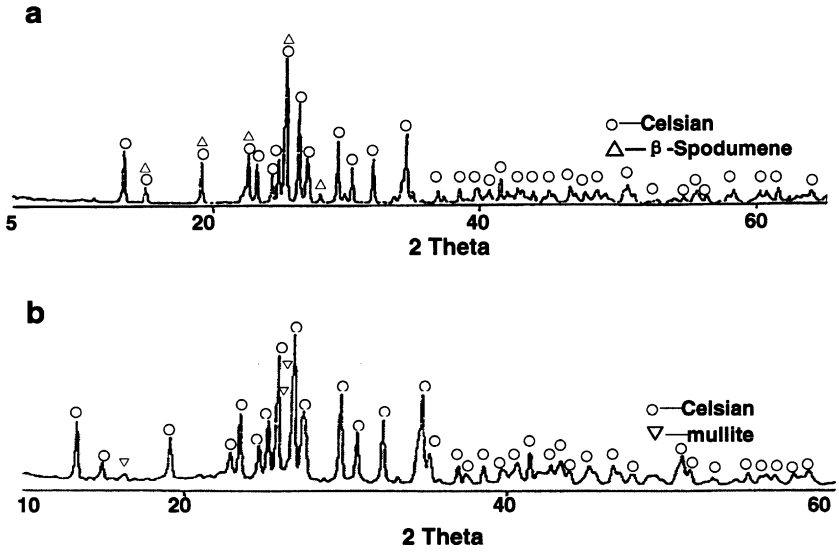


Fig. 4. XRD results of BAS glass after heat treatment at 1200 °C for 0.5 h: (a) with 3 wt.% $Li_2O$; (b) with 20 wt.% celsian seeds.

Table 2
Relative densities of $SiC_{pl}$/BAS composites

| $SiC_{pl}$ content (vol.%) | 0 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| Relative density (%) | 99.8 | 99.4 | 99.1 | 98.4 | 96.9 |

decreases with increasing SiC platelet content. The composites with different $SiC_{pl}$ content could be densified to 98% of the theoretical density except for the composites with 40 vol.% $SiC_{pl}$. SEM observations indicate that the distribution of SiC platelets is homogenous and the basal planes of the majority of the platelets are aligned in a prefered orientation perpendicular to the hot-pressing direction.

The results of XRD analysis show that the composites only contain $SiC_{pl}$ and BAS phase without other crystalline phases (Table 3). On the other hand, celsian was the predominant crystalline phase in the BAS matrix, indicating that the incorporation of 20 wt.% celsian seeds can effectively promote the hexacelsian- to celsian-$BaAl_2Si_4O_8$ transformation (as shown in Fig. 5). Previous investigation revealed that the hexacelsian to celsian transformation is very sluggish and the metastable hexagonal phase always exists below 1590 °C if no any additives.[11]

The microstructures of the composites are shown in Fig. 6. It could be seen that the SiC platelets have a good bond with the BAS matrix grains without obvious interfacial reaction or amorphous layer (Fig. 6a and b). In addition, some dislocations could be found at the interface between hexacelsian and celsian phase grains (Fig. 6c and d). They may be caused by the residual thermal mismach stress at their interface. As shown in Fig. 5 and Table 3, small amount of hexacelsian phase still exists in the BAS matrix, although celsian seeds can effectively promote its transformation to celsian. Since the hexacelsian phase has a much higher thermal expansion coefficient ($8\times10^{-6}$ °$C^{-1}$) than that of celsian phase ($2.29\times10^{-6}$ °$C^{-1}$), a large residual thermal stress will develop at their interface after cooling down from the sintering temperature.

Table 3
Summary of XRD analyses of $SiC_{pl}$/BAS composites

| Material | XRD phases |
|---|---|
| BAS matrix | Celisan, hexacelsian |
| 10 vol.% $SiC_{pl}$/BAS | β-SiC (*s*), celsian (*s*), hexacelsian (*vw*) |
| 20 vol.% $SiC_{pl}$/BAS | β-SiC (*s*), celsian (*s*), hexacelsian (*vw*) |
| 30 vol.% $SiC_{pl}$/BAS | β-SiC (*s*), celsian (*s*), hexacelsian (*vw*) |
| 40 vol.% $SiC_{pl}$/BAS | β-SiC (*s*), celsian (*s*), hexacelsian (*vw*) |

X-ray intensities: *s* = strong, *vw* = very weak.

### 3.4. Mechanical properties of $SiC_{pl}$/BAS composites

Fig. 7 a shows the flexural strength of the composites as a fraction of SiC platelet content. The strength of the composites increases with increasing SiC platelet content from 10 to 30 vol.%. It indicates that the load can effectively transfer from BAS matrix to SiC platelet due to the good BAS–$SiC_{pl}$ interfacial bonding. However, the strengthening effect of SiC platelets reduces with further increasing the content of platelets to 40 vol.%, the strength decreased from 181 MPa (in 30 vol.% $SiC_{pl}$/BAS composites) to 151 MPa. This may be attributed to the low relative density of 40 vol.% SiCpl/BAS composites (its relative density is only 96.9%).

A similar trend was observed in SENB fracture toughness of the BAS composites versus platelet content, as shown in Fig. 7b. By incorporation of 30 vol.% $SiC_{pl}$, the fracture toughness increased by 114%, from 1.49 MPa $m^{1/2}$ for the pure BAS matrix to 3.20 MPa $m^{1/2}$, indicating the good toughening effect of SiC platelets. The toughening mechanisms could be seen clarly from the observations of fracture surfaces and indentation crack paths, as shown in Figs. 8 and 9, repectively.

The fracture surfaces of the composites obtained after flexural strength tests are shown in Fig. 8. The fracture mode is intergranular for all platelet additions, indicating the presence of weak grain boundary structure suitable for crack deflection and pull-out. A significant change in roughness in the fracture surfaces of the composites was observed with increasing the volume

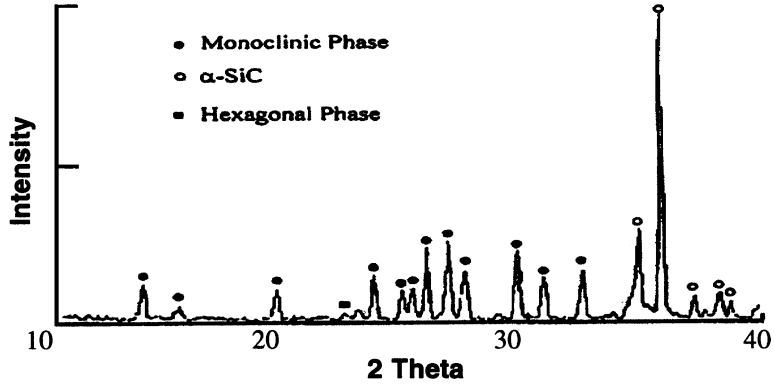


Fig. 5. XRD results of 40 vol.% SiCpl/BAS composite after sintering.

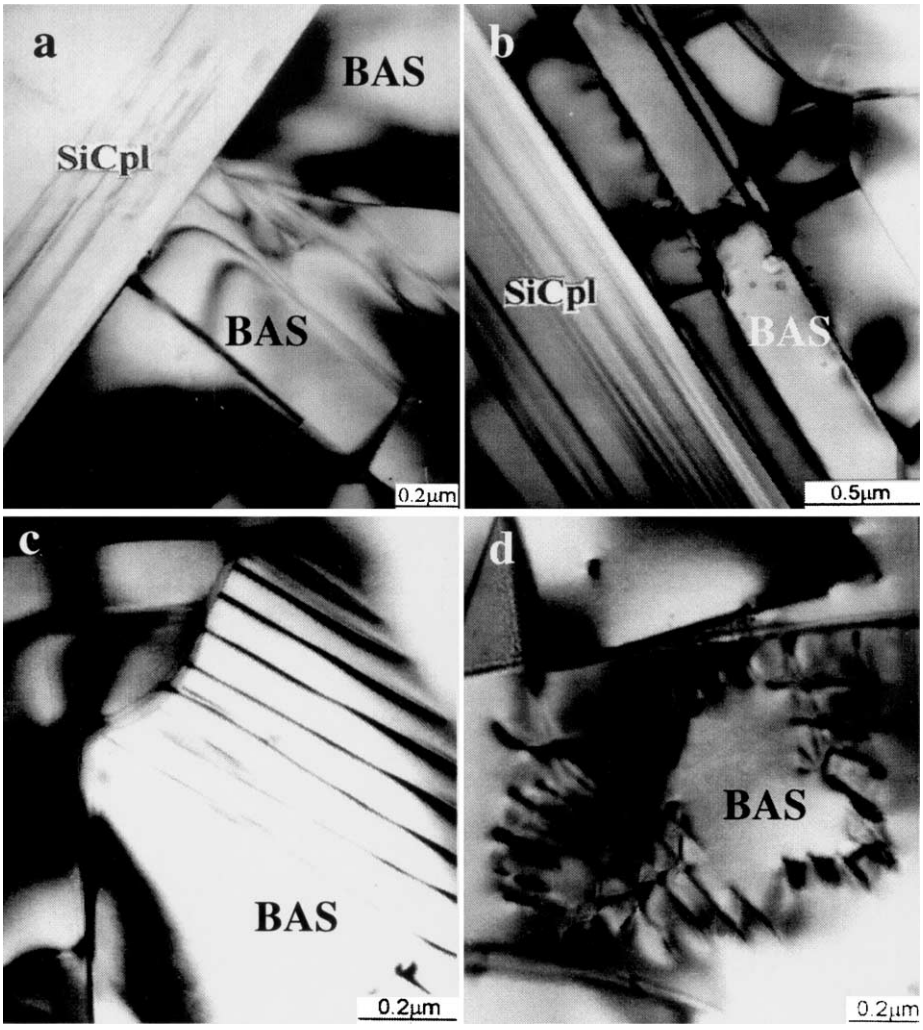


Fig. 6. Transmission electron micrographs of $SiC_{pl}$/BAS composites: (a), (b) showing that the SiC platelets are well bond to the BAS matrix grains; (c), (d) showing the dislocations at the interface between BAS matrix grains due to residual thermal stress at the interface.

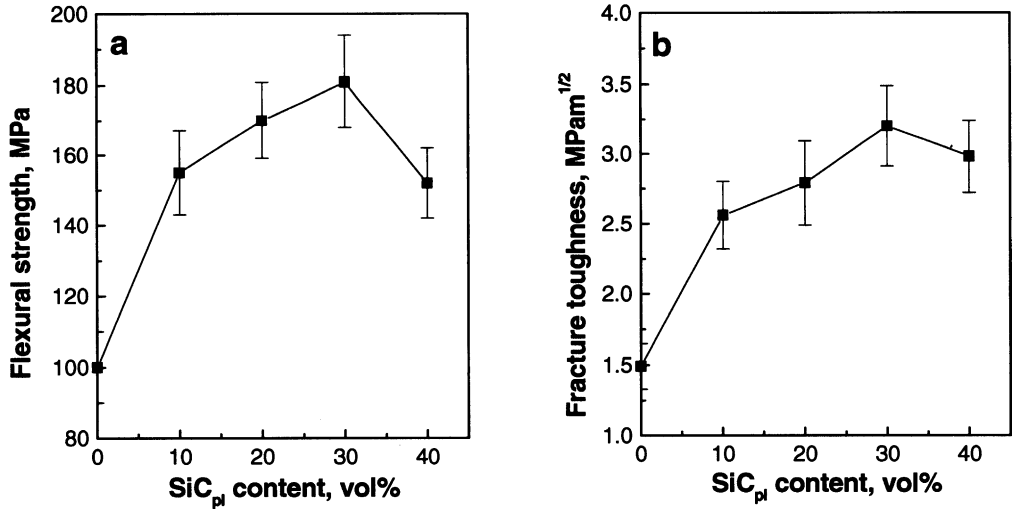


Fig. 7. Room temperature mechanical properties of $SiC_{pl}$/BAS composites as a function of SiC platelet content: (a) flexural strength, (b) fracture toughness.

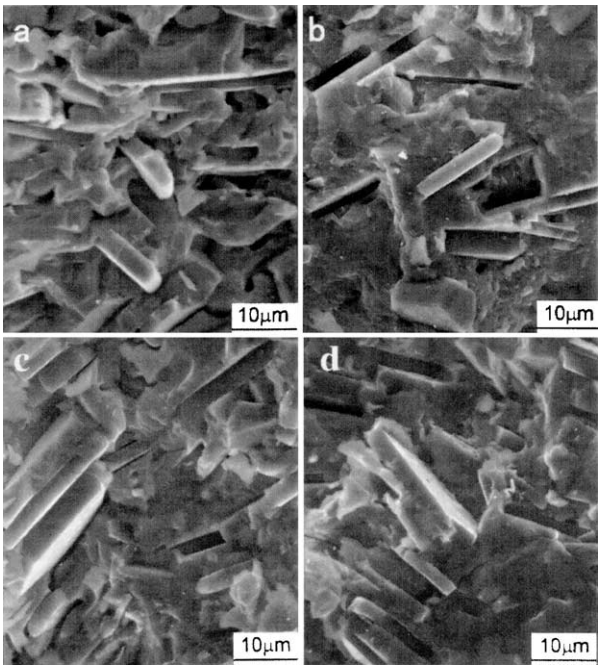


Fig. 8. SEM photographs of fractured surfaces of SiCpl/BAS composites: (a) 10 vol.% SiCpl/BAS; (b) 20 vol.% SiCpl/BAS (c) 30 vol.% SiCpl/BAS; (d) 40 vol.% SiCpl/BAS.

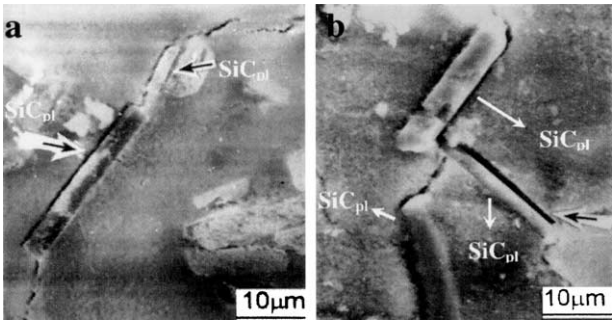


Fig. 9. SEM photographs of indentation crack paths in SiCpl/BAS composites: (a) crack deflected by platelets, (b) crack deflection and bridging by platelets.

fraction of plateletes. This was attributed to the crack deflection mechanism which was very effective in increasing the toughness. Furthermore, the presence of some holes further indicates that crack deflection by platelet took place during fracturing. The crack branching and deflection around the SiC platelets could be demonstrated more clearly by observing the crack propagation paths produced by Vickers indentation, as shown in Fig. 9.

As stated above, crack deflection is the main toughening mechanism in the investigated $SiC_{pl}$/BAS composites. But the effect of the residual thermal stress on the toughness can not be neglected. As the thermal expansion coefficient of the celsian matrix ($2.2\times10^{-6}\ ^{\circ}C^{-1}$) is much lower than that of SiC platelet ($8.9\times10^{-6}\ ^{\circ}C^{-1}$), this should result in a compressive stress in the celsian matrix during cooling from the sintering temperature. During propagating the crack through the fluctuating residual stress field, the crack front will prefer to reside in the region of compressive stress, and an extra externally applied stress intensity will therefore be required to cause continued crack propagation and hence increase of toughness will occur. Todd et al.[15] estimated the increment in toughness coursed by the compressive residual stresses in glass matrix reinforced with $Al_2O_3$ platelets, indicating a significant toughening effect from this source.

## 4. Conclusions

1. Homogenous and transparent gel glass of barium aluminosilicate was successfully synthesized by sol-gel method using TEOS, aluminum isoproponal and barium acetate;
2. Incorporation of 3 wt.% $Li_2O$ or 20 wt.% celsian seeds can effectively promote the formation of celsian and the transformation from hexacelsian to celsian;
3. The flexural strength and fracture toughness of $BaAl_2Si_2O_8$ glass-ceramic matrix can be greatly improved by addition of SiC platelets. By incorporation of 30 vol.% $SiC_{pl}$, the flexural strength and the fracture toughness of the composites increase 80% and 114% compared to the pure BAS matrix, respectively. The main toughening mechanism is crack deflection. The thermal residual stress in the BAS matrix may have also made a significant contribution to the fracture toughness of the composites, although this was not quantitatively investigated in this study.

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