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Effect of zirconia addition on crystallinity, hardness, and microstructure of gel-derived barium aluminosilicate, $BaAl_2Si_2O_8$

J. C. DEBSIKDAR[†], O. S. SOWEMIMO*
Idaho National Engineering Laboratory, PO Box 1625, Idaho Falls, ID 83415, USA

The effect of zirconia (ZrO_2) additions, in amounts equivalent to 5, 10, 20 and 40 mol %, to barium aluminosilicate, $BaAl_2Si_2O_8$, was studied by examination of the phase assemblage of the mixtures after crystallization heat treatments at ~ 1050 °C or more using X-ray diffraction (XRD). In all cases, $BaAl_2Si_2O_8$ gel crystallized into the hexacelsian polymorph. XRD results also indicated solid solubility of 10 mol % or more ZrO_2 in hexacelsian material. Precipitation of an additional phase, tetragonal ZrO_2, occurred in the $BaAl_2Si_2O_8$ material containing 20 mol % ZrO_2. Also, 95% and 99% dense celsian ceramics were fabricated at 1450 and 1580 °C sintering temperatures, respectively, using cold isostatically pressed pellets produced from powder mixtures containing 20 and 40 mol % ZrO_2. These pellets also contained 20 wt % gel-derived lithia-doped celsian "seed" powder to promote hexacelsian to celsian transformation during sintering. Indentation hardness values for the 99% dense celsian ceramic without and with 20 mol % ZrO_2 were 8.04 and 10.80 GPa, respectively. Scanning electron microscopy was used to examine the microstructures of these samples.

1. Introduction

Owing to its thermal stability up to ~ 1600 °C, the monoclinic form of barium aluminosilicate, $BaAl_2Si_2O_8$, known as celsian, is potentially an important matrix material for ceramic composites. Consequently, research is underway on producing celsian ceramic (from $BaAl_2Si_2O_8$ glass) by a glass-forming technique for ease of fabrication, and on development and control of microstructure through post-consolidation heat treatment for crystallization of the shaped glass to the desired celsian ceramic end-product. But synthetic $BaAl_2Si_2O_8$ glass, produced either by conventional melting [1] or by the sol–gel process [2], crystallizes into a hexagonal polymorph (hexacelsian) that is unsuitable for ceramic applications because of its ~ 3% volume change due to inversion at 300 °C. However, earlier work by Guillem Villar *et al.* [3] shows that the hexacelsian to celsian transformation can be effected in the 1000–1200 °C temperature range by the addition of certain mineralizers, namely Li_2CO_3, LiF, MoO_3 and TiO_2. The celsian to hexacelsian ratio was found to be a function of both the amount of the mineralizer and the heat-treatment temperature. Lithium compounds were found to be the most effective mineralizers.

Zirconia (ZrO_2) is one of the most common nucleating agents used for controlled nucleation and crystallization of glasses for producing glass-ceramics of uniform microstructures. Even though direct experimental evidence on the precise role of oxide nucleating agents is rather meagre, it has been reported that different phase assemblages, characterized by different sets of properties, can result from using the nucleating agent [4]. Moreover, the presence of the tetragonal form of zirconia (t-ZrO_2) as a second-phase material in ceramic composites improves their fracture toughness by structural transformation of t-ZrO_2, a phenomenon in which increased toughness is derived from the work required to stress-induce ZrO_2 from the tetragonal to the monoclinic (m-ZrO_2) structure in the vicinity of a propagating crack. Furthermore, m-ZrO_2 can also be a toughening agent where toughening is derived from the work required to produce and extend microcracks in the vicinity of a crack front. In materials that contain both t-ZrO_2 and m-ZrO_2, both phenomena (stress-induced transformation and microcracking) can contribute to fracture toughness [5]. The present work had two objectives: to study the crystallization behaviour of $BaAl_2Si_2O_8$ gel in the presence of ZrO_2 as the nucleating agent, and to examine the effect of phase assemblage and microstructure on the mechanical properties of ZrO_2 containing celsian ceramics. The results obtained so far are presented in this paper.

2. Experimental procedure

$BaAl_2Si_2O_8$ gel was synthesized according to the procedure reported earlier [2]. In short, the alkoxide

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[†] *Present address*: US Bureau of Mines, Tuscaloosa Research Center, Tuscaloosa, AL, USA.
* *Present address*: Clark Atlanta University, Atlanta, GA, USA.

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precursors were mixed together, refluxed at 105–110 °C, and then hydrolysed to prepare the gel. In the present study, the $BaAl_2Si_2O_8$ gel was calcined at 800 °C for 12 h in free-flowing oxygen to remove the organics. For each composition containing ZrO_2, organic-free X-ray amorphous powdered material was mixed with the calculated quantity of zirconium propoxide, $Zr(OC_3H_7)_4$, in isopropanol and hydrolysed with a 4 molar ratio of nanopure water to $Zr(OC_3H_7)_4$ to form a slurry. The slurry was dried in air at 70 °C and then calcined at 600 °C in free-flowing oxygen to remove any residual organics from the $Zr(OC_3H_7)_4$. The above procedure was used to produce $BaAl_2Si_2O_8$ materials containing 5, 10, 20, and 40 mol % ZrO_2.

Differential thermal analysis (DTA) at 10 °C min^{-1} heating rate was used to determine the crystallization temperatures of the $BaAl_2Si_2O_8$ gel material containing different mole percentages of zirconia. The crystallization heat treatments were conducted in an "EPD" furnace with a microprocessor controller (Kanthal Corporation, USA). The heat-treatment schedule consisted of 10 °C min^{-1} heating rate, 2 h hold at the predetermined temperature, and air quenching. The phase compositions of the materials were examined by X-ray powder defractometry (Philips PW 1729 automated diffractometer, scanning rate 1 °C min^{-1}).

For ceramic fabrication, the starting powder was a mixture of 800 °C-heated $BaAl_2Si_2O_8$ gel and 20 wt % gel-derived celsian [2]. Celsian powder was used as the "seed" material to promote hexacelsian to celsian phase transformation of the $BaAl_2Si_2O_8$ gel material during sintering. The above powder was mixed with different (calculated) quantities of $Zr(OC_3H_7)_4$, hydrolysed, dried, and calcined as described earlier. "Green" pellets, each ~ 12 mm diameter, were fabricated with these powders by cold isostatic pressing (CIP) at ~ 206 MPa (30×10^3 p.s.i.). Also, pellets were fabricated from $BaAl_2Si_2O_8$ material without ZrO_2. The latter samples were fabricated to generate baseline data. The "green" pellets were sintered at 1450 °C in a Lindberg box furnace. The sintering at 1580 °C was conducted in an alumina tube furnace designed and fabricated at the Idaho National Engineering Laboratory (INEL). In all cases the sintering schedule consisted of 10 °C min^{-1} heating rate, a 2 h hold at the sintering temperature, and 5 °C min^{-1} cooling rate.

The weight loss of the green pellets during sintering was determined gravimetrically. Pellet densities (both "green" and sintered) were determined from the weights and dimensions. The ceramic microstructures were examined by SEM (AMRAY 1830). An indentation technique [6, 7] was used to determine the hardness of selected samples using a Vicker's pyramidal diamond indentor. The pellets were ground to ensure parallel faces and polished to a 1 μm finish. The hardness was determined using a 0.98 N load applied for 15 s. Following load release, the dimensions of the surface indentation were measured optically. Hardness values were calculated using $H_v = AP/a^2$, where H_v is the Vicker's hardness number, A is a constant that depends on indentor geometry, P is the load on the indentor, and a is the length of the indent diagonal.

3. Results and discussion

The DTA exotherms corresponding to the crystallization of $BaAl_2Si_2O_8$ gel with and without the ZrO_2 additive are shown in Fig. 1. It is observed that crystallization of all the samples occurred in the 1050–1125 °C range for heating at 10 °C min^{-1}. However, the crystallization peak temperature, representing the maximum crystallization rate, decreased as the amount of ZrO_2 in the $BaAl_2Si_2O_8$ gel increased (Table I). These results seem to suggest that the ZrO_2 additive provided the heterogeneous nucleation sites (in the calcined gel structure) and thermodynamic excess free energy necessary for the increased rate of crystallization.

Our earlier study showed that alkoxy-derived ZrO_2 gel crystallizes to m-ZrO_2 (synthetic baddeleyite) at 1050 °C (Fig. 2). In the present work, we examined whether m-ZrO_2 phase is precipitated in the crystallized products of $BaAl_2Si_2O_8$ gel containing 5, 10 and 20 mol % ZrO_2 with a 1050 °C/20 h heat treatment. Moreover, several additional samples were produced by heating at 1300 °C for 2 and 20 h to examine change(s), if any, of phase composition of ZrO_2 in the products. The $BaAl_2Si_2O_8$ gel material containing 5 and 10 mol % ZrO_2 crystallized into the hexacelsian polymorph at 1050 °C and above, irrespective of the duration of the heat treatments. A typical XRD pattern of these materials is shown in Fig. 3. However, the composition containing 20 mol % produced an additional t-ZrO_2 phase (Fig. 4) corresponding to

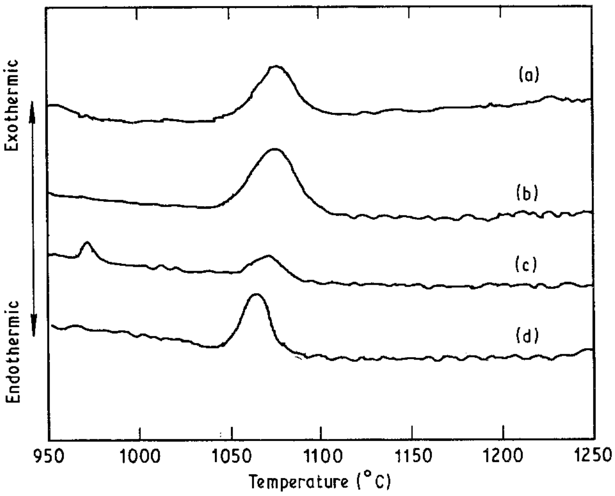

Figure 1 DTA curves corresponding to the crystallization exotherms of gel-derived $BaAl_2Si_2O_8$ containing different ZrO_2 contents (mol %).

TABLE I DTA peak temperature of the crystallization exotherms of $BaAl_2Si_2O_8$ gel containing ZrO_2 additive

Sample designation	Peak-temperature (°C)
BAS[a]	1094
BAS + 5 mol % ZrO_2	1081
BAS + 10 mol % ZrO_2	1072
BAS + 20 mol % ZrO_2	1069

[a] BAS = 800 °C-heated organic-free $BaAl_2Si_2O_8$ powder.

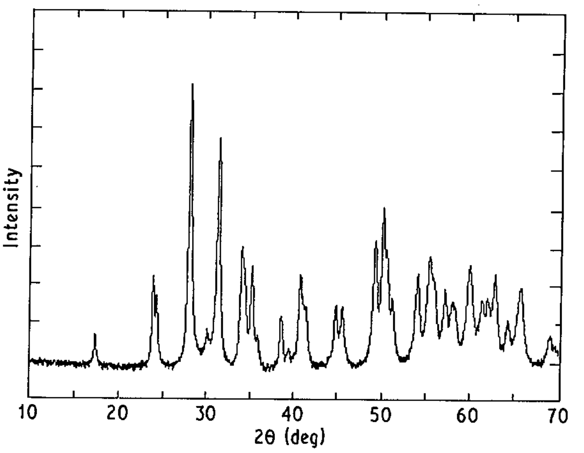

Figure 2 X-ray powder diffractogram of 1050 °C-heated zirconia gel.

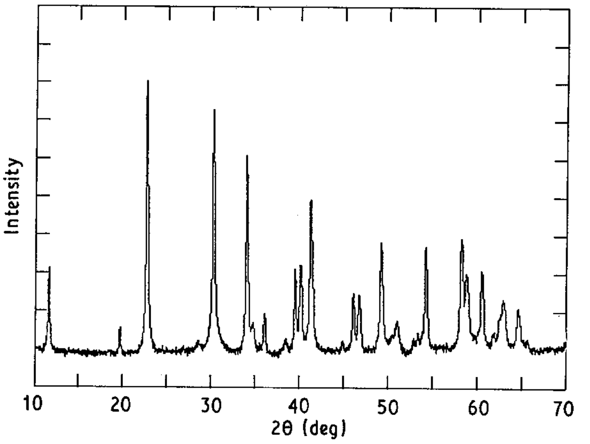

Figure 3 X-ray powder diffractogram of 1050 °C-heated $BaAl_2Si_2O_8$ containing 10 mol % ZrO_2.

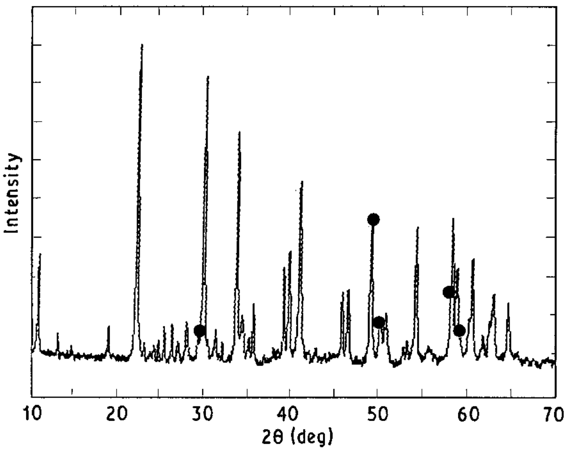

Figure 4 X-ray powder diffractogram of $BaAl_2Si_2O_8$ containing 20 mol % ZrO_2. (●) Tetragonal zirconia peaks.

JCPDS card no. 24-1164. The XRD results presumably indicate solid solubility of at least 10 mol % ZrO_2 in hexacelsian. However, a systematic study is required to establish the solid solubility limit of ZrO_2 in $BaAl_2Si_2O_8$. It may be mentioned here that the t-ZrO_2 precipitate in $BaAl_2Si_2O_8$ (Fig. 4) retained the tetragonal phase after the material was further heated for 20 h at 1100 °C (monoclinic phase field of ZrO_2), which perhaps indicates that the ZrO_2 crystallites in the material were extremely fine [4]. However, the fact that none of these samples showed any indication of the presence of the celsian suggests that ZrO_2 addition does not enhance hexacelsian to celsian transformation rate, at least up to the temperature of 1300 °C used in the present work.

The densities of the "green" and sintered pellets of $BaAl_2Si_2O_8$ seeded with 20 wt % gel-derived celsian and different mol % ZrO_2 are shown in Table II. As expected, the densities of the ceramics increased with increasing ZrO_2. Bansal and Hyatt [8] have determined the density of $BaAl_2Si_2O_8$ glass to be $3.22 \pm 0.003\ \mathrm{g\,cm^{-3}}$. Our density data show that in zirconia-containing celsian ceramics, approximately 95% and 99% (calculated) theoretical density can be produced at 1450 and 1580 °C sintering temperatures, respectively.

The gel-derived celsian powder used as the seed material for ceramic fabrication was synthesized by crystallization heat treatment of $BaAl_2Si_2O_8$ gel containing 5 wt % lithium oxide (Li_2O) [2]. It is well known that lithium can have deleterious effects on the mechanical properties of structural ceramics. However, because of its high-temperature volatility, some amount of lithium present in "green" ceramic bodies should be expected to volatilize during the sintering process. For this reason, we monitored weight-loss characteristics of "green" pellets, all of which contained 20 wt% celsian "seed" material, to determine the feasibility of producing alkali-free celsian ceramic. The weight-loss characteristics of the "green" pellets as a function of sintering temperatures are shown in Table III. Weight loss occurred from all the samples during the sintering step. Even though the lithium content in the "green" bodies was inversely proportional to the ZrO_2 content, the weight losses increased with increasing ZrO_2 content (Table III). The weight loss of the samples containing no ZrO_2 was a little over 0.5%, which presumably resulted largely from the loss of lithium-bearing species even though some loss could also be due to traces of residual organics and/or structural water (i.e. residual –OH groups in 800 °C-heated $BaAl_2Si_2O_8$ gel structure) [9, 10]. However, the greater weight losses of ZrO_2-containing samples are most likely related to the residual carbon derived from the zirconium alkoxide precursor (in addition to lithium loss) and, as such, the losses were approximately proportional to the amount

TABLE II Densities of $BaAl_2Si_2O_8$ ceramics

Sample designation	Green density ($\mathrm{g\,cm^{-3}}$)	Sintered density ($\mathrm{g\,cm^{-3}}$)	
		1450 °C	1580 °C
BAS*[a]	2.30	3.06	3.17
BAS* + 5 mol % ZrO_2	2.34	3.09	3.25
BAS* + 20 mol % ZrO_2	2.42	3.18	3.34
BAS* + 40 mol % ZrO_2	2.47	3.40	3.51

[a] BAS* = Organic-free $BaAl_2Si_2O_8$ material containing 20 wt% gel-derived celsian powder [2].

TABLE III Weight-loss characteristics of celsian ceramics during sintering

Sample designation	Li_2O content (%) (introduced as mineralizer in celsian "seed" powder	Weight loss during sintering (%)	
		1450 °C	1580 °C
BAS*[a]	1.00	0.55	0.61
BAS* + 5 mol % ZrO_2	0.98	0.56	0.60
BAS* + 20 mol % ZrO_2	0.92	0.94	0.96
BAS* + 40 mol % ZrO_2	0.82	1.18	1.20

[a] BAS* = organic-free $BaAl_2Si_2O_8$ material containing 20 wt % gel-derived celsian powder [2].

of zirconium alkoxide in the precursor powders. These weight loss data (Table III), however, indicate that complete removal of lithium could not be achieved at 1580 °C sintering (of the lithium-doped precursor material) for producing celsian compounds and that calcination of zirconium alkoxide-doped $BaAl_2Si_2O_8$ materials at 600 °C was inadequate for complete removal of the organics. Because the presence of lithium in the ceramics can have deleterious effects on their mechanical properties, further studies should be conducted to determine the critical minimum amount of lithium-doped celsian seed material required for complete transformation of the gel-derived $BaAl_2Si_2O_8$ material into celsian ceramic.

The phase composition of the two selected ceramics was studied to examine whether the addition of celsian seed material was effective in transforming the $BaAl_2Si_2O_8$ gel completely into the celsian-phase ceramic material. Fig. 5 compares the XRD patterns of seeded and unseeded compositions, both containing 20 mol % ZrO_2 and sintered at 1450 °C. The XRD pattern of the seeded composition fully corresponds with that of the celsian phase ceramic. The results clearly demonstrate that organic-free amorphous $BaAl_2Si_2O_8$ gel material mixed with 20 wt % or less celsian seed particles, could be used as the precursor material for fabricating celsian ceramics. Therefore, the present sol–gel approach has the potential to eliminate the need for fabricating $BaAl_2Si_2O_8$ glass at high temperature and crystallization heat treatment of the ground glass prior to ceramic fabrication. Consequently, the sol–gel method might be more cost effective than present fabrication processes for producing celsian-based monoliths and composites.

The indentation hardness of a selected sample of 1580 °C-sintered celsian ceramic was 8.04 GPa, whereas the hardness of a selected sample containing 20 mol % ZrO_2 (sintered at the same temperature), 10.80 GPa, was approximately 35% greater. These results clearly show that the strength of celsian ceramics can be significantly increased by the addition of zirconia. The microstructural features of these two samples are shown in Figs 6 and 7. It is evident that addition of zirconia changed the microstructure of the celsian ceramic substantially. It appears that the

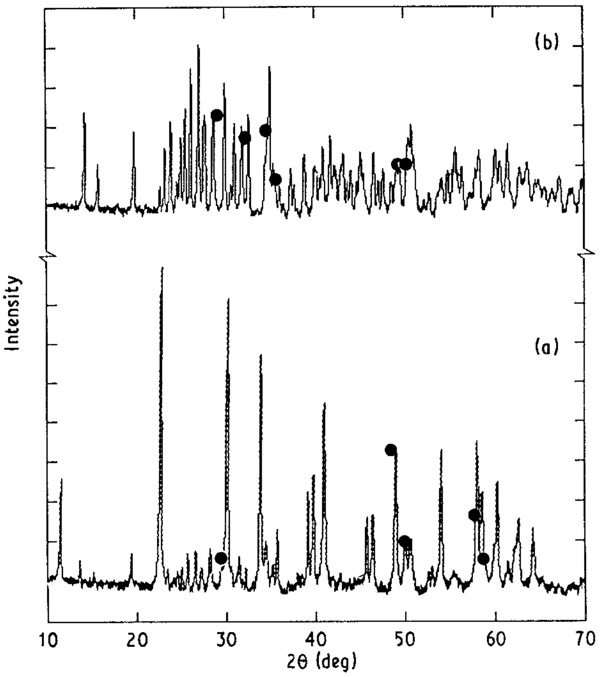

Figure 5 X-ray powder diffractogram of $BaAl_2Si_2O_8$ ceramic with 20 mol % zirconia. (a) Precipitation of tetragonal zirconia (●) in hexacelsian matrix; and (b) 20 wt % celsian "seed" particles, showing precipitation of tetragonal zirconia (●) in celsian matrix.

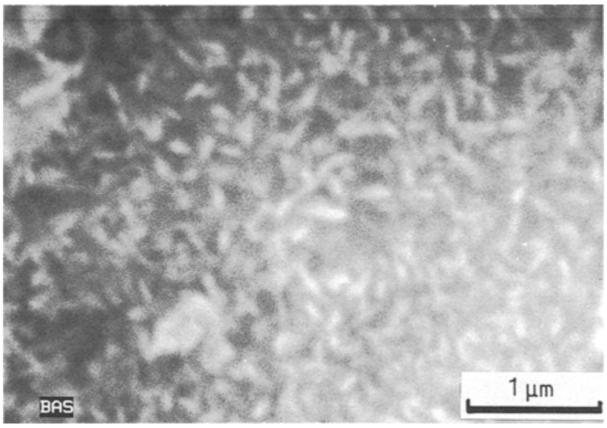

Figure 6 Scanning electron micrograph showing the microstructure of celsian ceramic material.

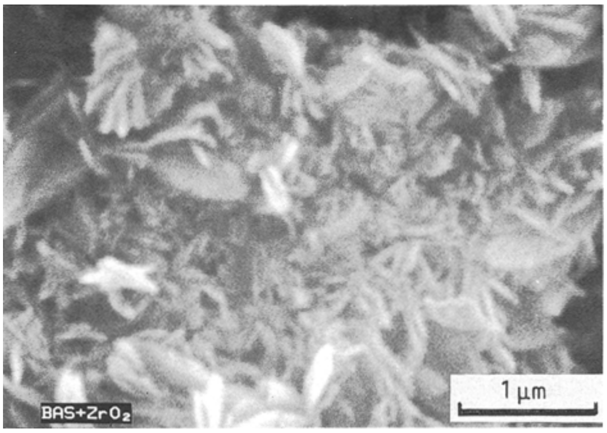

Figure 7 Scanning electron micrograph showing the microstructure of celsian ceramic containing 20 mol % ZrO_2.

microstructural changes contributed to the improved hardness of the zirconia-containing celsian ceramic, as did the presence of t-ZrO_2. Future work will involve a systematic study to determine the optimum ZrO_2 content for producing celsian ceramics with maximum strength and toughness.

4. Conclusions

The following conclusions can be drawn from the results of the present investigation.

1. The crystallization rate of $BaAl_2Si_2O_8$ gel to hexacelsian phase increased with increasing zirconia content. However, zirconia was not effective in hexacelsian → celsian phase transformation up to 1300 °C heat treatment.
2. The solid solubility of zirconia in hexacelsian was of the order of 10 mol % or more. However, tetragonal zirconia precipitated out in the material containing 20 mol % sol–gel zirconia.
3. Celsian ceramics can be fabricated from organic-free amorphous $BaAl_2Si_2O_8$ sol–gel material mixed with an appropriate amount of celsian seed particles. Approximately 95% and 99% dense zirconia-containing celsian ceramics were produced at 1450 and 1580 °C sintering temperatures, respectively.
4. The indentation hardness of a sol–gel derived celsian monolithic ceramic was 8.04 GPa. The hardness increased to 10.80 GPa (i.e. approximately 35%) on the addition of 20 mol % zirconia.

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References

1. D. BAHAT, *J. Mater. Sci.* **5** (1970) 805.
2. J. C. DEBSIKAR, *J. Non-Cryst. Solids*, to be published.
3. M. C. GUILLEM VILLAR, C. GUILLEM MONZONIS and J. ALARCON NAVARRO, *Trans. J. Brit. Ceram. Soc.* **82** (1983) 69.
4. W. D. KINGERY, H. K. BOWEN and D. R. UHLMAN (eds), "Introduction to Ceramics", 2nd Edn (Wiley, New York, 1976), pp. 368–80.
5. F. F. LANGE, N. E. CLAUSSEN, in "Ultrastructure Processing of Ceramics, Glasses, and Composites", edited by Larry L. Hench and Donald R. Ulrich (Wiley, New York, 1984) pp. 493–506.
6. B. R. LAWN and E. R. FULLER, *J. Mater. Sci.* **10** (1975) 2016.
7. R. H. MARION, in "Fracture Mechanics Applied to Brittle Materials", ASTM STP 678, edited by S. W. Feiman (American Society for Testing and Materials, Philadelphia, PA, 1979) pp. 103–11.
8. N. P. BANSAL and M. J. HYATT, "Crystallization Kinetics of $BaO\text{-}Al_2O_3\text{-}SiO_2$ Glasses", report no. NASA TM-101964, prepared for the 90th Annual Meeting of the American Ceramic Society, Cincinnati, OH, 1–5 May 1988.
9. J. C. DEBSIKDAR, M. R. PASCUCCI, H. S. MURALIDHARA and R. R. WILLS, "Exploratory Development of Fused Silica Laser Window", final report to AFWL, Kirtland Air Force Base (Contract C5004), 25 February 1985.
10. J. C. WALCK and C. G. PANTANO, "Sol–Gel Processing and Crystallization of Yttrium Alumino Silicate", report no. MTL TR 90-10, submitted to the US Army Laboratory Command, Adelphi, MD 20783, March 1990.

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