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Ceramics International 36 (2010) 1589–1596
CERAMICS INTERNATIONAL
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Glass–ceramics and composites containing aluminum borate whiskers

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Received 2 December 2009; received in revised form 15 January 2010; accepted 17 February 2010
Available online 25 March 2010

Abstract

Glass–ceramics and composites containing aluminum borate whisker crystals were developed using two different approaches: crystallization of an aluminum borosilicate glass or addition of an aluminum borate precursor powder to a glass frit. Two different glass frits were used, a commercially available borosilicate glass or the same aluminum borosilicate glass used in the crystallization experiments. X-ray diffraction analysis showed that $Al_4B_2O_9$ or $Al_{18}B_4O_{33}$ whiskers formed in all samples, indicating that the glass crystallized significantly with increasing heating temperature, and that the precursor can be effectively be used to generate *in situ* aluminum borate crystals within glass matrices. However, the samples produced by mixing the aluminum precursor with glass frits contained porosity after processing, indicating that pressureless viscous sintering was not efficient. The hardness of the glass–ceramic did not vary significantly with processing temperature, but the (indentation) fracture toughness measured showed a >100% increase (after heating at 1200 °C), demonstrating that whisker-shaped crystals are effective in increasing the mechanical toughness of the glass matrix. The hardness of the composites showed a dependence on the amount of aluminum borate crystals present.

Keywords: B. Whiskers; D. Glass; D. Glass ceramics; Aluminum borate; Crystallization

1. Introduction

The introduction of fibers and whiskers to reinforce glasses and ceramics can lead to significant improvements in their mechanical properties, such as increased fracture toughness, bending strength, hardness and thermal shock resistance [1]. However, the possibility of using whiskers is limited due to the health hazard posed by loose particles with a high aspect ratio shape, although the infiltration of whisker preforms can reduce the problem [2]. Textured ceramics by templated grain growth can also be produced, although processing requires carefully controlled conditions [3,4]. The *in situ* direct growth of whiskers in a glass, analogous to the creation of fluorcansite platelets in toughened glass–ceramics, is an attractive alternative method. Unfortunately, the number of oxide systems that can be exploited are limited, as oxide whiskers are usually produced by vapor–solid phase reactions [5,6]. Very recently, the formation and crystallization behavior of glasses in the Al_2O_3–B_2O_3–SiO_2 system has been investigated, demonstrating that whisker-shaped aluminum borate crystals can be obtained after thermal treatment [7–9].

Currently, aluminum borate whiskers are successfully used as reinforcement for aluminum or magnesium metal matrix composites, leading to increased tensile strength and elastic modulus, and reduced thermal expansion coefficient [10,11]. They can be produced using precursors such as nitrates, sulfates, alkoxides or hydroxides or by direct reaction of oxides [12–14]. Aluminum borate is a refractory compound (melting point 1440 °C) possessing excellent physical properties, such as low density (2.94 g/cm^3), high hardness (7 in the Mohs scale), a high Young's modulus (400 GPa) and high electrical resistivity that has also been used to fabricate dense or porous ceramics [15–17].

In this paper, we describe the production of whisker-reinforced glass ceramics by using two different approaches: (a) the *in situ* crystallization of an aluminum borosilicate glass and (b) the *in situ* development, within a glass matrix, of aluminum borate whiskers derived from a chemical precursor.

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doi:10.1016/j.ceramint.2010.02.039

2. Experimental procedure

An aluminum borosilicate glass (ABS), containing barium and magnesium oxides as modifiers, was obtained from reagent grade SiO_2, Al_2O_3, B_2O_3, MgO and $BaCO_3$. The composition of the glass was: 48.8 B_2O_3–24.4 SiO_2–17.0 Al_2O_3–4.9 BaO–4.9 MgO (mol%). After thorough mixing, the batch (100 g) was melted in a high-alumina crucible at 1500 °C for 30 min (heating rate 10 °C/min), and then poured into a stainless steel mold and annealed at 550 °C for 8 h. 4 mm thick slices of the glass were heat treated at 800–1200 °C for 2 h in an electric furnace (heating rate 2 °C/min) to produce glass–ceramics samples. Some selected glass samples were heat-treated using a microwave process, but the resulting microstructures were comparable to the conventionally heated glasses.

The prepared glass was also was milled in a vibration mill, and then sieved (325 mesh) to obtain the glass powder for the preparation of glass–matrix composites. Commercially available aluminum borate hydrate ($2Al_2O_3{\cdot}B_2O_3{\cdot}3H_2O$, Fischer Scientific, Pittsburgh, PA) was used as a precursor for aluminum borate whiskers. Glass–matrix composites were produced by mixing either the prepared aluminum borosilicate glass or a borosilicate glass (7070, Corning, NY) with different amounts of the precursor, which was previously calcined at 600 °C for 2 h to remove the hydration water. Based on the density values reported in the literature for the aluminum borate phases, the amount of precursor was adjusted to produce two different volumetric percentages of crystals within the glass matrix (see Table 1).

Pellets (diameter 1.3 cm, thickness 0.3 cm) were produced by unixaxial pressing (100 MPa) using an acrylate binder, and were subjected to heat treatments from 800 to 1200 °C for 2 h (heating rate 2 °C/min) to produce composite samples.

Selected samples were analyzed by differential thermal analysis and thermogravimetric analysis (DTA-TGA, SDT 2690, TA Instruments, New Castle, DE, powders of different particle size, 10 °C/min), dilatometry (Netzsch 402E, 10 °C/min), X-ray diffraction (XRD, Scintag PADV and X_2 diffractometers, Scintag Inc., Cupertino, CA), Scanning Electron Microscopy (SEM, Hitachi S-300H, Hitachi High-Technologies Co., Tokyo, Japan; to better investigate the crystallized phase morphology, some samples were also etched in 10 vol% HF for 1 min at room temperature). The microhardness and the fracture toughness were measured on polished samples using micro-indentation (Leco Model V1-100-C1, LECO Corp., St. Joseph, MI, Vickers tip; 500 g load for microhardness, 2 kg load toughness determination). The porosity of the samples was computed from bulk density and pycnometer (MicroMeritics AccuPyc 1330, Micromeritics Instrument Corp., Norcross, GA) measurements.

3. Results and discussion

3.1. Glass–ceramics

The composition of the glass was designed taking into account the results of recent investigations, which indicated that a high B_2O_3/SiO_2 ratio favors crystallization, and that BaO and MgO oxides improve the glass formation and influence the morphology of the aluminum borate whiskers [7–9]. This glass composition yielded a homogeneous, transparent glass after melting. DTA/TGA and dilatometric analysis (see Fig. 1a and b) revealed that the glass transition temperature (T_g) was 590 °C, the dilatometric softening point (T_s) was 640 °C, while a well defined crystallization peak (T_{cryst}) was present at 755 °C (see Table 1); a small endothermic peak was also present at 1040 °C, corresponding to the phase transformation from $Al_4B_2O_9$ to $Al_{18}B_4O_{33}$.

To identify the dominant crystallization mechanism in the ABS glass, i.e. surface or bulk crystallization, we applied DTA measurements to glass powders of different size [18–20]. This method allows one to identify the crystallization behavior of a glass by plotting two parameters (namely $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ *vs* the particle size of glass powder. $(\delta T)_p$ is the maximum height of the peak occurring at the crystallization temperature T_p in the DTA pattern, and $(\Delta T)_p$ is the peak width at half maximum. Fig. 2a reports the DTA curves for different particle size of the ABS glass, and it shows that there is little influence of the particle surface area on the crystallization tendency. The variation of the $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ parameters as a function of particle size for ABS glass is shown in Fig. 2b. Both $(\delta T)_p$ and $T_p^2/(\Delta T)_p$ decreased with increasing particle size, indicating that bulk crystallization is the dominant mechanism in this glass [18,19].

The ABS glass samples deformed only slightly during the crystallization heat treatments (see Fig. 3a). In fact, the dilatometric curve for the glass (see Fig. 1b) shows that shrinkage (i.e. viscous flow) stops at around 745 °C, which

Table 1
Main characteristics of the produced alumino-borosilicate glass and composition of the composite samples.

Sample	T_g (°C)	T_s (°C)	T_{cryst} (°C)	CTE ($\times10^{-6}$ °C^{-1}, 20–550 °C)	CTE ($\times10^{-6}$ °C^{-1}, 750–1000 °C)
7070 glass	495	~560	–	3.2	–
ABS glass	590	640	755	5.1	49.0

Composite samples	Glass type	Glass vol%	Aluminum borate whiskers (vol%)
CS1	7070	50	50
CS2	7070	70	30
CS3	ABS	70	30

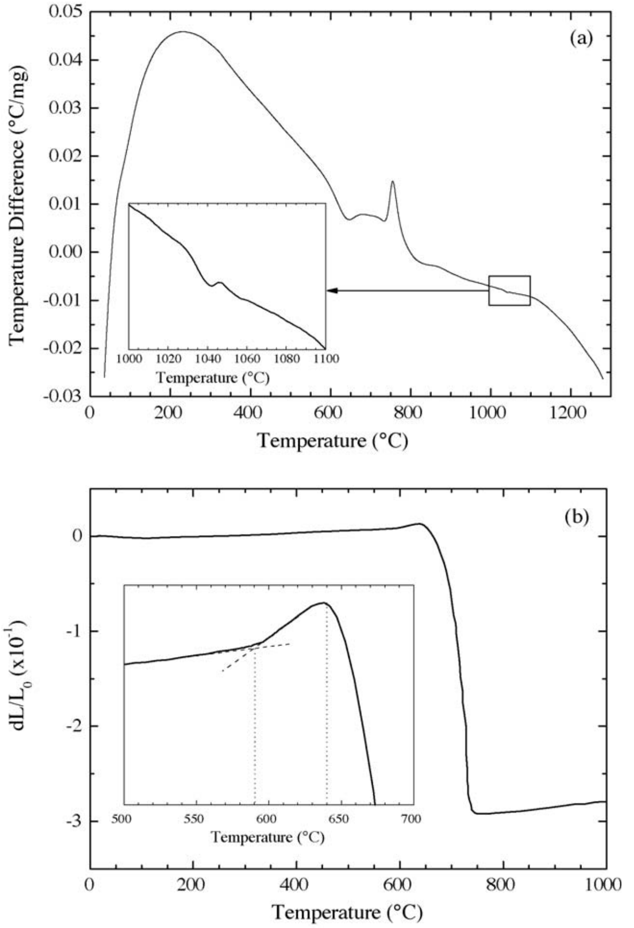

Fig. 1. (a) DTA and (b) dilatometric curves for ABS glass.

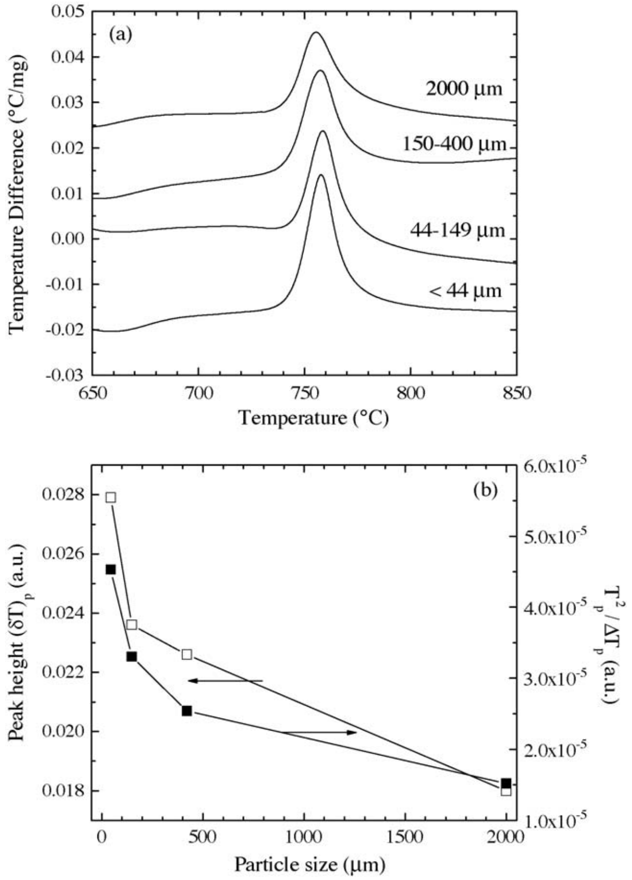

Fig. 2. (a) DTA curves for ABS glass powders of different size and (b) crystallization parameters ($(\delta T)_p$, $T_p^2/(\Delta T)_p$) as a function of particle size for ABS glass.

corresponds to the onset of crystallization (Fig. 1a). After crystallization, the coefficient of thermal expansion (CTE) of the material changed from 5.1 to $49.0 \times 10^{-6}\,C^{-1}$ (Table 1).

The amount and type of crystallites formed depended on the heat treatment temperature (Fig. 3a) with some residual glass always present in the heat-treated materials (see Fig. 3b). In fact, on the basis of the composition of the glass and assuming that only the high temperature aluminum borate crystal phase would form, it is possible to compute that a maximum molar percentage of crystals of ~25.5% could be expected at 1200 °C. At temperatures between 800 and 1100 °C, $Al_4B_2O_9$ (JCPDS-ICSD, PDF#29-0010) was the only phase, while at 1200 °C $Al_{18}B_4O_{33}$ (JCPDS-ICSD, PDF#29-0009) was also present, in accordance with the phase diagram [16] Actually, the $Al_{18}B_4O_{33}$ phase is expected to form at ~1040 °C from the decomposition of $Al_4B_2O_9$ [15] but the diffraction data clearly showed the presence of $Al_4B_2O_9$ up to 1100 °C (note that, in refs. [8,9], a similar XRD diffraction pattern was attributed to a different phase, $Al_{20}B_4O_{36}$, which however was never found or identified in any other papers dealing with the synthesis and characterization of aluminum borate-based materials (and does not appear in the JCPDS 2008 database). It is likely that the lower temperature phase of aluminum borate is retained to higher temperatures (in the glass ceramic) because of limited mass transport between the glassy phase and the transforming whiskers. In the case of the aluminum borate precursors (the powders), boron oxide evolution can occur without such a kinetic limitation.

SEM images of the fracture surface (Fig. 4a, sample heat treated at 1200 °C) showed the presence of some residual porosity (due to incomplete refining of the melt) and, after etching in HF, a large amount of highly interconnected crystalline whiskers became visible. At 1000 °C, the whiskers had a diameter of 0.12 ± 0.04 μm and a length of 2–4 μm, and their diameter did not significantly change after processing at 1200 °C, although their amount increased and some rod-like crystals started to appear (Fig. 4b and c).

3.2. Composites

DTA/TGA analysis of the aluminum borate precursor (not reported here for the sake of brevity), showed that in the 50–400 °C temperature range there was a continuous weight loss associated with a broad endothermic effect centered at 180 °C, which can be attributed to the loss of structural water from the compound. At 780 °C an exothermic effect occurred, with an associated 6 wt% weight loss, corresponding to the crystallization of the $Al_4B_2O_9$ phase. The total weight loss was

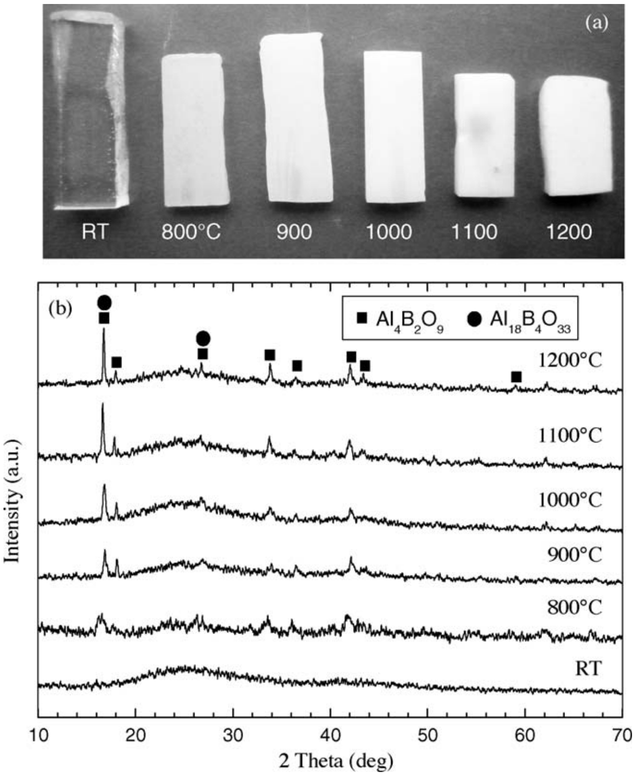

Fig. 3. (a) Appearance and (b) X-ray diffraction patterns of ABS glass samples after annealing and heat treated at different temperatures.

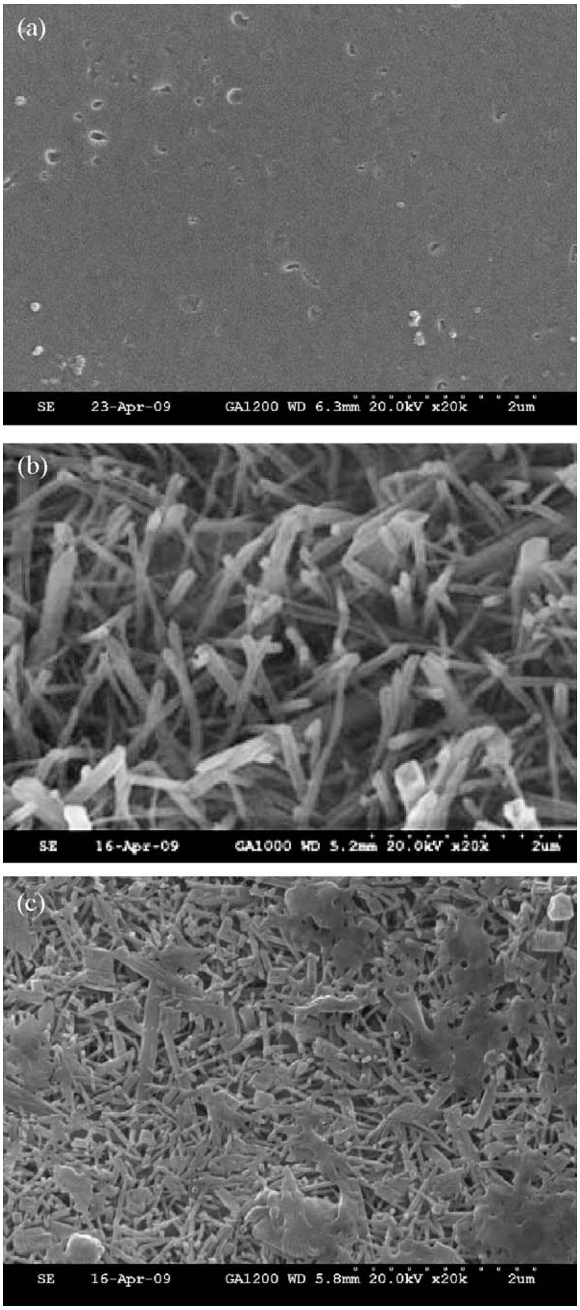

Fig. 4. SEM micrographs of: (a) ABS glass heat treated at 1200 °C (no etching); (b) ABS glass heat treated at 1000 °C (after etching) and (c) ABS glass heat treated at 1200 °C (after etching).

38 wt% at 1200 °C, with a further 1 wt% loss taking place in the 1400–1550 °C interval, probably due to the vaporization of some boron oxide (melting point of $Al_{18}B_4O_{33}$ is reported to be 1440 °C) [15]. Heating of the aluminum borate precursor pellets led to the formation of an interconnected network of whisker-shaped crystals (see Fig. 5) of sub-micron size (diameter 0.04 ± 0.01 μm; length ~0.5 μm) for heat treatments up to 1000 °C and larger, more rod-like crystals and with a lower aspect ratio, for heat treatments of 1100 and 1200 °C (diameter 1.0 ± 0.16 μm; average length ~8 μm at 1200 °C). X-ray diffraction analysis confirmed the formation of the $Al_4B_2O_9$ phase at low temperatures, and its complete transformation to $Al_{18}B_4O_{33}$ above 1040 °C (Fig. 6). Furthermore, no residual phases (such as B_2O_3 or Al_2O_3) were present at any of the processing temperatures, indicating that the stoichiometry of the precursor was correct for the production of aluminum borate via direct solid state reactions between aluminum and boron oxide-based species mixed at the molecular level.

Heat treatment of the composite pellets (containing a glass mixed with the calcined precursor for aluminum borate whiskers) produced materials with different amounts of crystallinity. In particular, the presence of aluminum borate crystals were produced at each processing temperature in the composite made using the 7070 glass (Fig. 7a and b) indicated that no adverse reactions occur between the precursor and the glass matrix occurred during heating. We conclude, therefore, that this precursor material can be successfully used for the *in situ* formation of whisker-shaped crystals in a glass matrix. Furthermore, it has to be noted that cristobalite did not form during processing of the borosilicate glass powder at any temperature, and no residual $Al_4B_2O_9$ phase could be detected in CS1 and CS2 samples heated at 1200 °C. The absence of cristobalite formation is in accord with earlier results which showed that aluminum borate inhibits the precipitation of crystalline silica [21].

Mixing of the ABS glass powder with the aluminum borate precursor resulted in samples possessing a higher degree of crystallinity than in the 7070 borosilicate glass, as indicated by

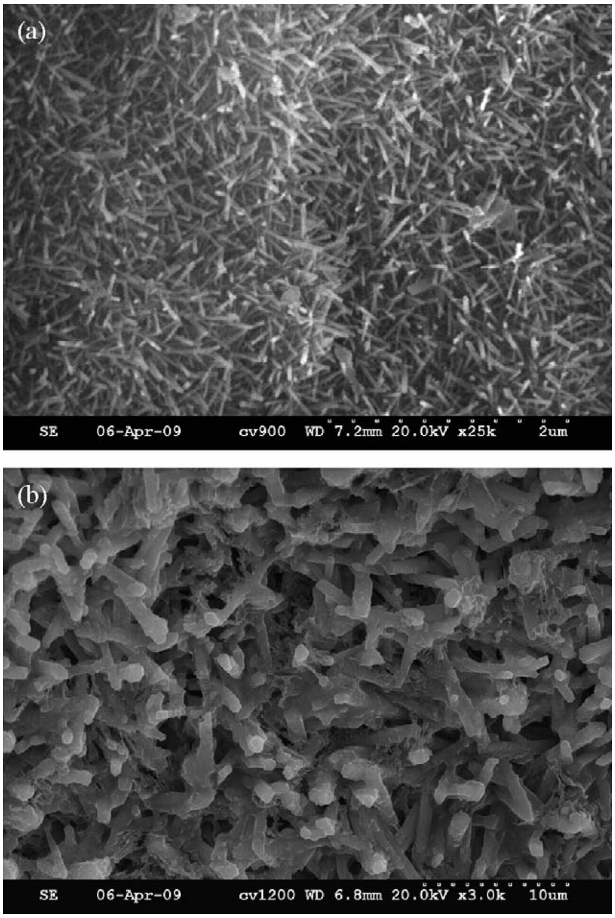

Fig. 5. SEM micrographs of: (a) aluminum borate precursor heat treated at 1000 °C for 2 h and (b) aluminum borate precursor heat treated at 1200 °C for 2 h.

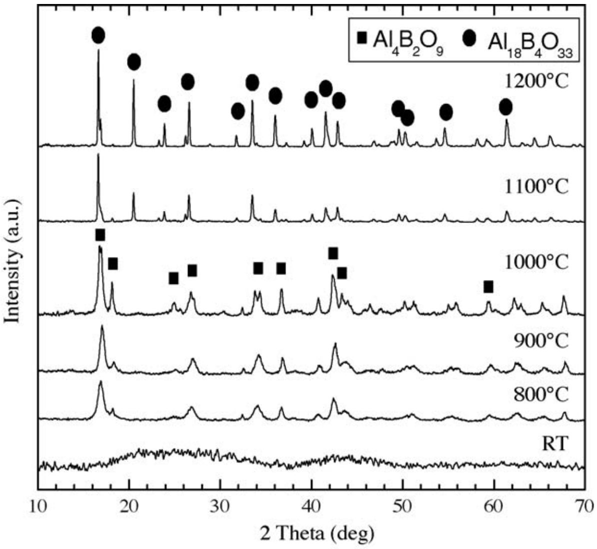

Fig. 6. X-ray diffraction patterns of aluminum borate precursor at room temperature and heat treated at different temperatures.

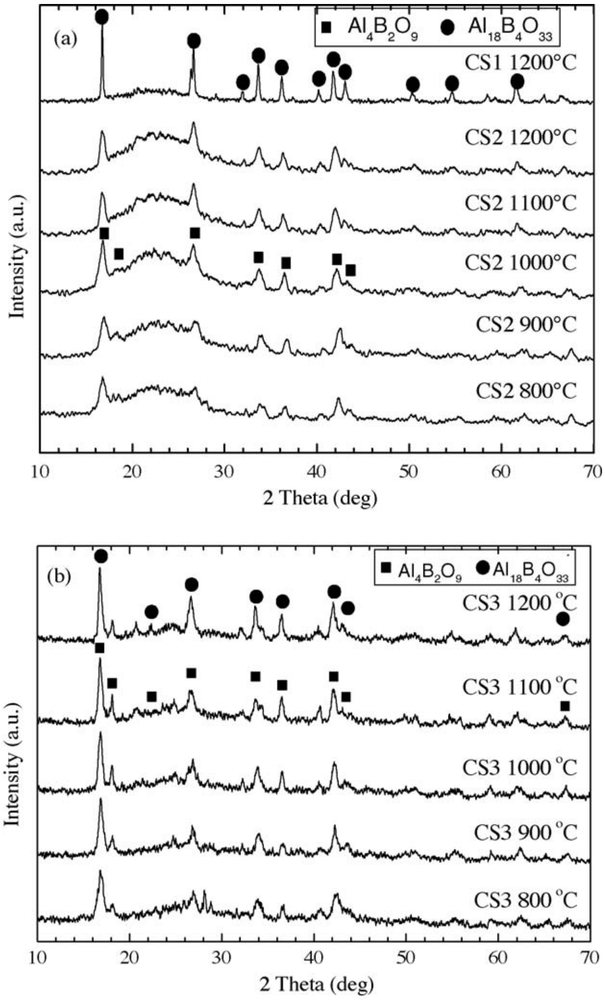

Fig. 7. X-ray diffraction patterns of composite samples heat treated at different temperatures: (a) CS2 (and CS1 1200 °C) and (b) CS3.

the smaller amorphous hump at ~23° (Fig. 7b), which is linked to the presence of an amorphous silicate phase. As observed for pure ABS glass, some residual $Al_4B_2O_9$ was present after the high temperature treatments (1100 and 1200 °C). The percent crystallinity of CS1, CS2, CS3 and Glass ABS samples heated at 1200 °C was estimated to be 62, 42, 53, and 16 vol% respectively, as determined by the analysis of the X-ray diffraction patterns [22].

In both the 7070 borosilicate and ABS glass composites, the presence of residual porosity and absence of sample deformation suggests that viscous flow was hindered by the presence of the interconnected network of crystals produced by the crystallization of the aluminum borate precursor [23]. In the 7070 borosilicate glass composites, the total porosity ranged from ~51 to ~49 vol% for CS1 samples heated at 800 and 1200 °C, and from ~38 to ~45 vol% for CS2 samples heated at 800 and 1200 °C, respectively. The situation was more complex for sample CS3, because the ABS glass crystallizes upon heating; i.e., the ABS glass crystallization temperature and dilatometric softening point are quite close to each other (separated by ~110 °C). This limits the possibility of successfully producing dense samples via sinter-crystallization [24]. In fact, the ''sinter-crystallization process'' (i.e., viscous sintering with concurrent crystallization) depends on a delicate balance between viscous flow

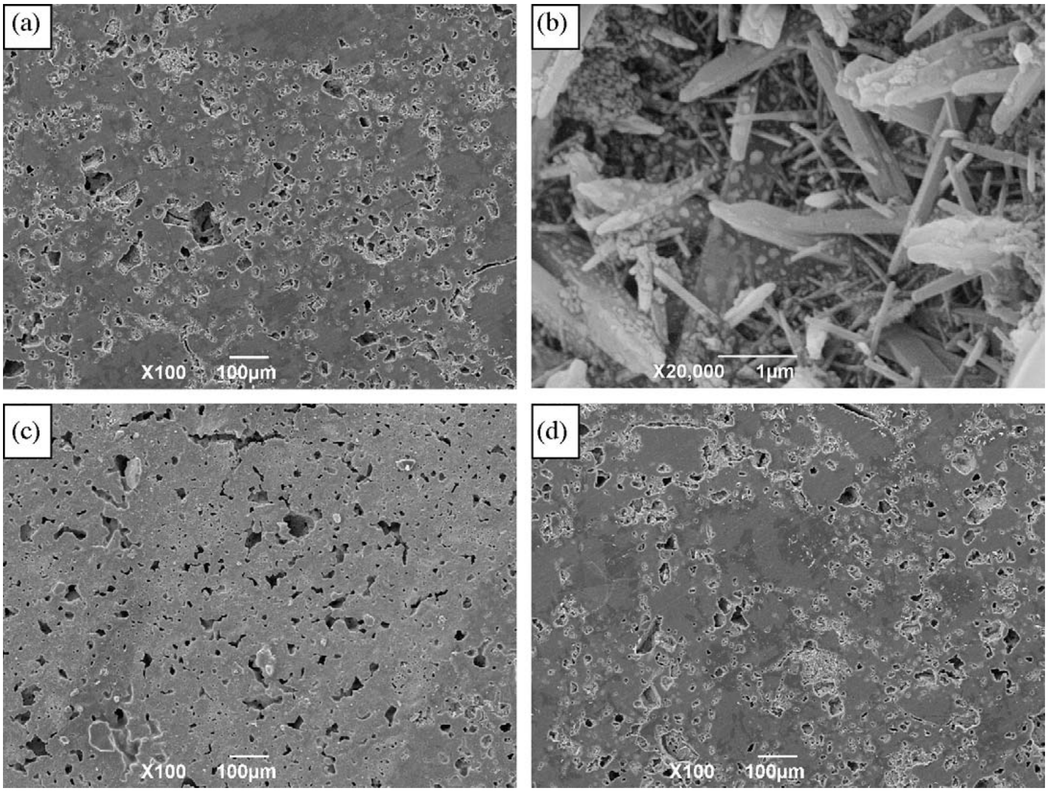

Fig. 8. SEM micrographs of composite samples. (a) Sample CS1; (b) detail of the inside of a pore (sample CS1); (c) sample CS2 and (d) sample CS3.

sintering and crystallization, the latter being further promoted by the high surface area of fine powders. If crystallization is dominant over viscous flow at the processing temperatures selected, crystal inclusions will greatly increase the viscosity of the glass, thus hindering sintering [23].

Some attempts were made to reduce the amount of residual porosity, which for samples CS3 was ~40 and ~27 vol% after heating at 800 and 1200 °C. For instance, pressed glass powders were directly inserted at 1200 °C, following the procedure suggested in the literature [25]. In another experiment, a sample was heated for 4 h treatment at 700 °C, followed by heating at 1200 °C (10 °C/min). In fact, a significant viscous flow is typically present already at a temperature of 50–100 °C beyond the dilatometric softening point (see also Fig. 1b) [26]. These experiments did not succeed in increasing the linear shrinkage occurring in the samples upon heating (a measure of viscous sintering), which was 11.1% for CS3 heated at 2 °C/min at 1200 °C to 8.9% for CS3 directly inserted at 1200 °C and 10.8% for CS3 heated at 700 °C and then 1200 °C (all samples were heated for 2 h). In Fig. 8 are reported the SEM images of the polished surface of samples CS1, CS2 and CS3. All the samples display the presence of distributed porosity, with an average size typically below 30 μm, with occasional larger cavities. A higher magnification image from the inside of a pore of sample CS1 shows the presence of a large amount of aluminum borate crystals protruding from the glass matrix.

Preliminary data for the mechanical properties of the glass–ceramic and composite samples were obtained by micro-indentation measurements. In Fig. 9a are reported the hardness values as a function of the heating temperature for both the glass–ceramic and glass–matrix composite samples. The heat treatment temperature led to an increase in hardness for the composite samples, because of the growth of hard aluminum borate crystals (aluminum borate has a hardness value which is about twice that of Pyrex glass, and similar to quartz [27]), and the average value indeed depended on the amount of aluminum borate precursor used (samples CS2 and CS3 had a similar average hardness, which was lower than that of sample CS1). The hardness of the ABS glass decreased with crystallization, possibly because of the change in composition of the glass matrix. Fracture toughness data were obtained by indentation using the standard procedure found in the literature [28]. Unfortunately, the presence of excessive residual porosity in the composite samples yielded inconsistent data, which are therefore not reported in Fig. 9b. In order to fully evaluate the mechanical properties of composite samples, pressure-assisted viscous sintering should be applied to fabricate dense samples. Conversely, the length of the cracks observed at the corners of the indents in the ABS glass–ceramics clearly decreased with increasing processing temperature, and therefore toughness was improved. Crystallization of the aluminum borate whiskers inside the glass led to a significant increase in toughness ranging from ~63% at 800 °C to ~113% at 1200 °C (see Fig. 9b).

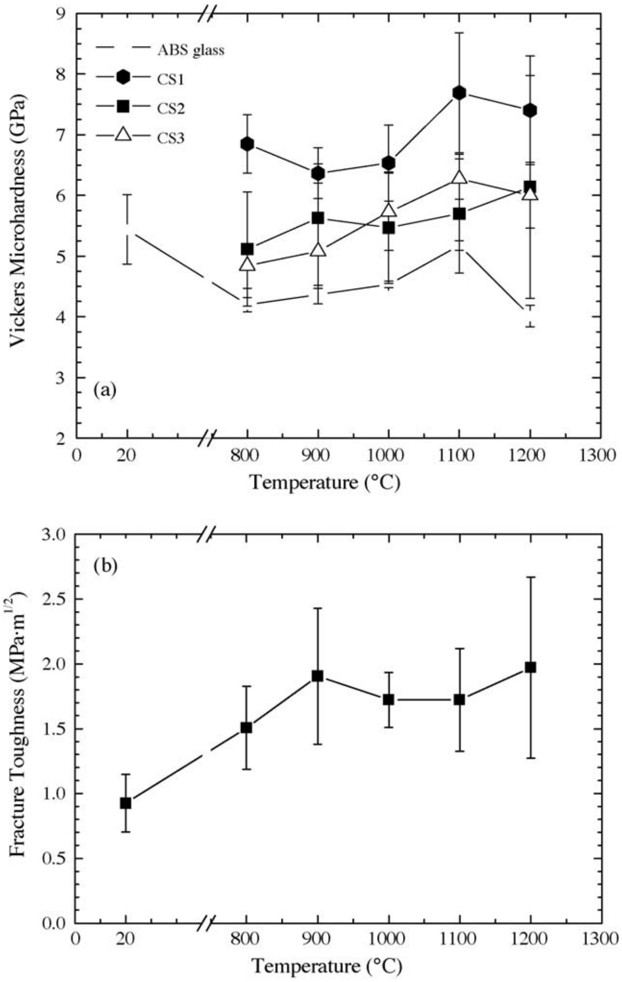

Fig. 9. (a) Hardness of ABS glass and composite samples heat treated at different temperatures and (b) fracture toughness of ABS glass before and after crystallization.

4. Conclusions

The designed and synthesized aluminum borosilicate glass crystallized via a bulk crystallization mechanism, producing an increasing amount of aluminum borate whiskers with increasing heating temperature. The creation of crystalline whiskers within the glass matrix yielded a 110% increase in fracture toughness, while the hardness was not significantly affected.

The aluminum borate precursor powders transformed into $Al_4B_2O_9$ or $Al_{18}B_4O_{33}$ whiskers, depending on the processing conditions. Mixing of the precursor powder with glass frits enabled the fabrication of composites containing aluminum borate whiskers embedded in a glass matrix. However, the composite materials produced by pressureless sintering possessed residual porosity, because viscous sintering was hindered by the presence of crystalline inclusions. The hardness of the composite materials increased with processing temperature and the amount of borate precursor used.

Acknowledgements

S.Z. gratefully acknowledges the International Internship in Materials (IIM) program of the Department of Materials Science and Engineering and the NSF International Materials Institute on New Functionality for sponsoring his research at Penn State.

References

[1] P.F. Becher, C.-H. Hsueh, P. Angelini, T.N. Tiegs, Toughening behavior in whisker-reinforced ceramic matrix composites, J. Am. Ceram. Soc. 71 (1988) 1050–1061.

[2] N.A. Travitzky, Mechanical properties and microstructure of mullite whisker-reinforced magnesium aluminosilicate glass with cordierite composition, J. Mater. Sci. Lett. 17 (1998) 1609–1611.

[3] I. Erkin Gonenli, G.L. Messing, Texturing of mullite by templated grain growth with aluminum borate whiskers, J. Eur. Ceram. Soc. 21 (2001) 2495–2501.

[4] C. Duran, Y.K. Tur, Processing and mechanical properties of textured mullite/zirconia composites, J. Eur. Ceram. Soc. 27 (2007) 1463–1467.

[5] S. Hashimoto, A. Yamaguchi, Synthesis of $MgAl_2O_4$ whiskers by oxidation–reduction method, J. Am. Ceram. Soc. 79 (1996) 491–494.

[6] K. Okada, N. Otuska, Synthesis of mullite whiskers and their application in composites, J. Am. Ceram. Soc. 74 (1991) 2414–2418.

[7] T. Sun, H. Xiao, Y. Cheng, H. Liu, Effects of MO (M = Ba, Mg, Ca) on the crystallization of B_2O_3–Al_2O_3–SiO_2 glass–ceramics, Ceram. Int. 35 (2009) 1051–1055.

[8] Y. Cheng, H. Xiao, B. Tang, Non-isothermal crystallization kinetics of MgO–BaO–B_2O_3–Al_2O_3–SiO_2 glass, Ceram. Int., doi:10.1016/j.ceramint.2009.05.010, in press.

[9] Y. Cheng, H. Xiao, C. Shuguang, B. Tang, Structure and crystallization of B_2O_3–Al_2O_3–SiO_2 glass, Phys. B 404 (2009) 1230–1234.

[10] L. Wang, J. Hu, Z.J. Li, W.D. Fei, Fracture behavior of aluminum borate whisker-reinforced aluminum alloy 6061 composite, Mater. Sci. Eng. A 497 (2008) 358–362.

[11] W.D. Fei, Y.B. Li, Effect of NiO coating of whisker on tensile strength of aluminum borate whisker-reinforced aluminum composite, Mater. Sci. Eng. A 379 (2004) 27–32.

[12] L.M. Peng, X.K. Li, H. Li, J.H. Wang, M. Gong, Synthesis and microstructural characterization of aluminum borate whiskers, Ceram. Int. 32 (2006) 365–368.

[13] C. Cheng, X.X. Ding, F.J. Shi, Y. Cheng, X.T. Huang, S.R. Qi, C. Tang, Preparation of aluminum borate nanowires, J. Cryst. Growth 263 (2004) 600–604.

[14] E.M. Elssfah, H.S. Song, C.C. Tang, J. Zhang, X.X. Ding, S.R. Qi, Synthesis of aluminum borate nanowires via a novel flux method, Mater. Chem. Phys. 101 (2007) 499.H–504.H.

[15] H. Scholze, Űber Aluminiumborate, Z. Anorg. Allg. Chem. 284 (1955) 272–277.

[16] S.B. Ray, Preparation and characterization of aluminum borate, J. Am. Ceram. Soc. 75 (1992) 2605–2609.

[17] J.X. Li, T. Narita, J. Ogawa, M. Wadasako, In situ synthesis of porous ceramics with a framework structure of aluminium borate whisker, J. Mater. Sci. 33 (1998) 2601–2605.

[18] C.S. Ray, Q. Yang, W. Huang, D.E. Day, Surface and internal crystallization in glasses determined by differential thermal analysis, J. Am. Ceram. Soc. 79 (1996) 3155–3160.

[19] C.S. Ray, D.E. Day, Indentifying internal and surface crystallization by differential thermal analysis for the glass-to-crystal transformations, Thermochim. Acta 280/281 (1996) 163–174.

[20] M. Romero, M. Kovacova, J.Ma. Rincón, Effect of particle size on kinetics crystallization of an iron-rich glass, J. Mater. Sci. 43 (2008) 4135–4142.

[21] J.-H. Jean, S-.P. Hwang, Preparation and characterization of low-dielectric glass composite with aluminum borate, Jpn. J. Appl. Phys. 33 (1994) L1472–L1474.

[22] S.M. Ohlberg, D.W. Strickler, Determination of percent crystallinity of partly devitrified glass by X-ray diffraction, J. Am. Ceram. Soc. 45 (1962) 170–171.

[23] A.R. Boccaccini, On the viscosity of glass composites containing rigid inclusions, Mater. Lett. 34 (1998) 285–289.

[24] E. Bernardo, G. Scarinci, E. Edme, U. Michon, N. Planty, Fast-sintered Gehlenite glass–ceramics from plasma-vitrified municipal solid

waste incinerator fly ashes, J. Am. Ceram. Soc. 92 (2009) 528–530.

[25] E. Bernardo, Fast sinter-crystallization of a glass from waste materials, J. Non-Cryst. Sol. 354 (2008) 3486–3490.

[26] A. Ray, A.N. Tiwari, Compaction and sintering behaviour of glass–alumina composites, Mater. Chem. Phys. 67 (2001) 220–225.

[27] H.N. Baumann, C.H. Moore, Electric furnace boroaluminate, J. Am. Ceram. Soc. 25 (1942) 391–394.

[28] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, A critical evaluation of indentation techniques for measuring fracture toughness. I. Direct crack measurements, J. Am. Ceram. Soc. 64 (1981) 533–538.