Journal of the European Ceramic Society 20 (2000) 1923–1928

Co-enhanced SiO_2-BN ceramics for high-temperature dielectric applications

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Received 1 February 2000; received in revised form 2 April 2000; accepted 8 April 2000

Abstract

Two typical high-temperature dielectric materials, fused silica and BN, have been used to form a composite with an attempt to overcome their own drawbacks. In the resultant BN–SiO_2 composites, BN platelike grains were preferentially orientated by hot pressing and homogeneously distributed in the fused silica matrix. An evident co-operative enhancement has been achieved by the combination of the constituents. The sinterability and the thermal shock resistance of the BN materials were increased and the ablation surface temperature was decreased by the involvement of the fused silica. On the other hand, the strength, fracture toughness, and flame ablation resistance of the fused silica were increased due to the addition of BN. Furthermore, an amorphous Si–B–O–N structure was identified in the surface layer of the ablated composites, to which attention should be further paid in the development of new elevated temperature dielectric materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: BN; Composites; Dielectric applications; Hot pressing; Mechanical properties; SiO_2-BN; Ablation

1. Introduction

Materials for radome and antenna windows are very important to the control of spacecraft. The harsh re-entry environment requires the materials to possess a number of critical properties, such as good mechanical and dielectric properties, excellent thermal shock resistance and very high ablation resistance. Fused silica and BN ceramics are two popular materials for such applications.

Fused silica is used because of its rather low and stable dielectric constant, a very low loss tangent, an extremely low coefficient of thermal expansion, a high chemical stability, and a high melting point.[1] However, its mechanical properties (mainly strength and toughness) and thermal ablation resistance are insufficient to meet the requirements of advanced re-entry vehicles. Silica glass fibers and Nextel polycrystal fibers (containing SiO_2, Al_2O_3 and B_2O_3) have been employed to reinforce the fused silica.[2,3] Although the rain-erosion resistance has been increased and the desirable dielectric property has been retained, the effects on mechanical properties and ablation resistance are not evident because of poor performance of the fibers. In other reports, the mechanical properties of the fused silica are greatly enhanced by the introduction of SiC fibers or carbon fibers,[4,5] but the dielectric properties are deteriorated because of the poor dielectric properties of the reinforcements. Therefore, it is of great significance to identify an appropriate reinforcement, which can effectively enhance the mechanical properties and the ablation resistance, but does not degrade the dielectric properties of the fused silica.

The h-BN ceramic is commonly used as a radar window material because it has a very low dielectric coefficient of 5.16, a low loss tangent of $10{\sim}11\times10^{-4}$ at room temperature,[6] a very high sublimation temperature of about 3000°C (no melting point), and good machinability. However, monolithic BN ceramic suffers from signal attenuation and thermal shock damage during the re-entry of high-speed vehicles.[7] The attenuation of signals is due to the high surface temperature and the low temperature gradient in the ablation surface area, as a result of the high sublimation point and the high thermal conductivity of the material, respectively.[7] The thermal shock damage is mainly attributed to its relatively high coefficient of thermal expansion (as compared with that of fused silica). Hence, the main issues for BN are to reduce its surface temperature, coefficient of thermal expansion and thermal conductivity, and to improve its sinterability. A US patent[8] offered a solution to these problems by means

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PII: S0955-2219(00)00107-2

of a composite containing a BN yarn reinforcement, a BN matrix and a SiO_2 filler. However, the fabrication process is rather complicated and time-consuming because it is difficult to incorporate a H_3BO_3 solution and a SiO_2 sol into the BN yarn pre-form and to convert these into BN and SiO_2, respectively.

Here, it is attempted to develop a relatively simple method to combine BN and fused silica into a composite, so as to overcome their own property drawbacks and to avoid the complexity in fabrication, e.g. as encountered in Ref. 8. It is expected that the toughness and ablation resistance of the fused silica can be improved by the addition of BN, making use of the layered structure and the high sublimation temperature of BN. On the other hand, the poor thermal shock resistance, low temperature gradient and high surface temperature of the BN, can be eased by means of the relatively low coefficient of thermal expansion, low conductivity and low melting point of the fused silica. In the present study, a series of BN–SiO_2 composites were fabricated via a powder-sintering route. The microstructure, mechanical and thermal ablation properties were characterised using a range of techniques. The results are discussed in relation to specific applications in space vehicles.

2. Experimental procedures

A series of BN–SiO_2 composites were processed by hot pressing of ($BN+SiO_2$) powder blends ranging from 15 to 90 vol.% BN, with a composition interval of 15 vol.%. Quartz glass and BN powders were used as the starting materials. The quartz glass powder was fully amorphous, with particles around 5–30 μm in diameter and SiO_2 content $\geqslant$99.9%. BN powder was of a partially crystallised (or turbulent) structure, containing BN (wt.%) 99.3%, B 0.13%, B_2O_3 0.44%, Na_2O 0.14%, and traces of Fe_2O_3 and NiO, with a grain size of 1–15 μm. A proprietary hot pressing procedure was employed. Microstructure of the processed materials was investigated by means of XRD, SEM, TEM and FT-IR. The flexural strength was measured by the three point bending method with specimen dimensions of $36\times4\times3$ mm^3, a bending span of 30 mm, and a crosshead speed of 0.5 mm/min. The fracture toughness (K_{IC}) was determined by the single-edge notched beam (SENB) method, with a specimen dimension of $24\times4\times2$ mm^3, an outer span of 16 mm, and a crosshead speed of 0.05 mm/min. The thermal ablation property was studied on an ablation equipment with the kerosene and liquid oxygen as the heating source. The linear ablation rates (defined as the thickness loss per unit time) were used as the criterion of ablation resistance of the materials. The temperature of the ablation surface was measured with a pyrometer.

3. Results and discussion

The sintered composites showed very high relative densities ranging from 93 to 99%, which increased with increasing SiO_2 content, or with decreasing BN content; this simply reflects the sinterabilities of the two constituent materials. The amorphous state of the fused silica was retained (see Fig. 1), which is very important in maintaining its low coefficient of thermal expansion, high thermal shock resistance, and good mechanical properties. It may be seen from Fig. 1 that the crystal structure of BN was also unchanged, and there does not appear any reaction between the fused silica and the BN, indicating good chemical compatibility. The above crystalline structures were also confirmed by their electron diffraction patterns [Fig. 2(c)]. TEM observations [Fig. 2(a)] showed that the fused silica formed a continuous phase in the composites. This means the viscous flow of the fused silica occurred during hot pressing, and the high relative densities of the composites should be attributed to this viscous flow. BN maintained its original grain morphology [Fig. 2(d)] and existed as a dispersed phase. It was noted that the phase boundaries were not clear, and there were no micro-cracks or separation at the interface between the fused silica and the BN. This is ascribed to the infiltration of the fused silica into the BN particles during hot pressing, and to the similarity of the coefficients of thermal expansion of these two phases.

The variations of mechanical properties of the composites with BN contents are shown in Fig. 3. It can be seen that the bending strength and fracture toughness showed their maximums at the same BN content of 60 vol.%. The decrease in the mechanical properties when BN > 60 vol.% is likely due to the reduction in the relative density. It was noted that the strength and the toughness of the fused silica were greatly enhanced by the addition of BN. For example, the bending strength and

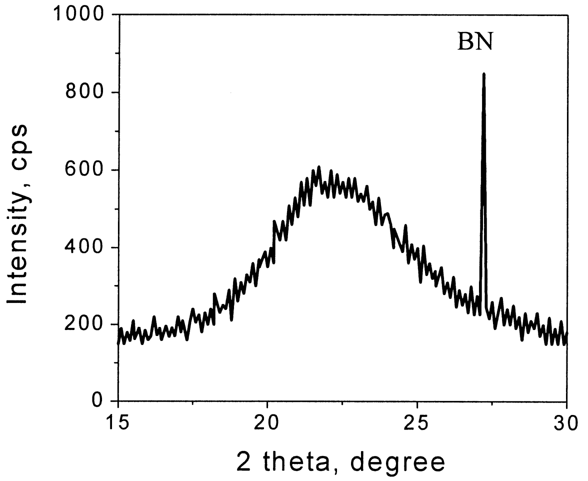

Fig. 1. XRD pattern of the BN–SiO_2 composite with 30 vol.% BN.

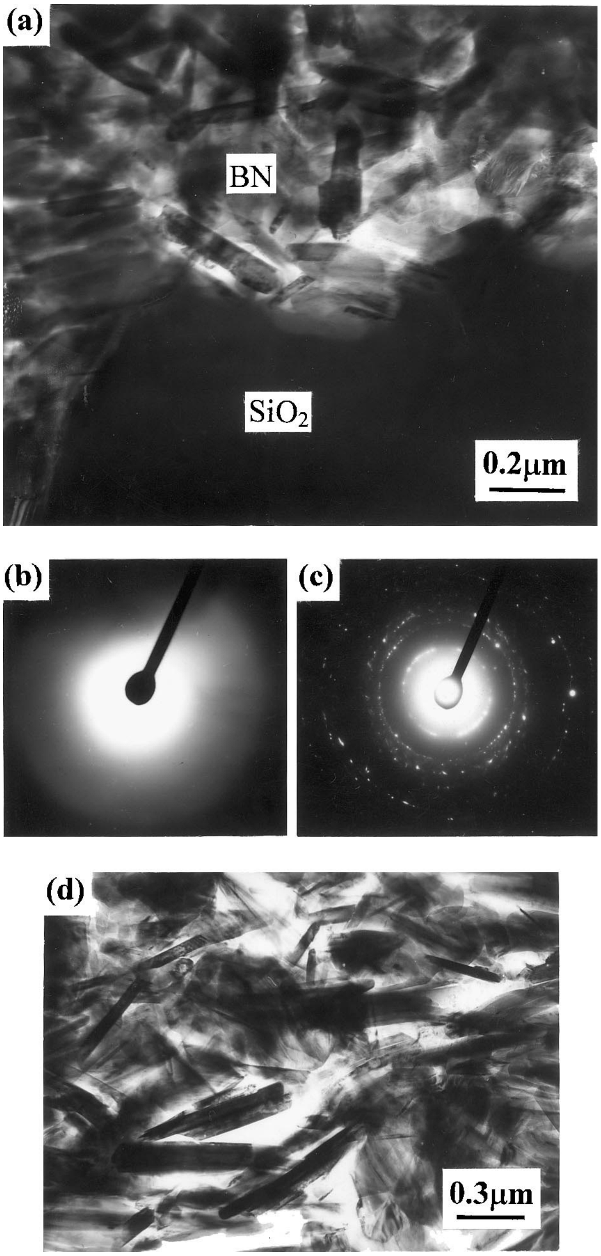

Fig. 2. TEM images of the composite with 30 vol.% BN, showing: (a) microstructure around a BN and SiO_2 interface; (b) electron diffraction pattern of the fused silica; (c) electron diffraction pattern of the BN; (d) crystal morphology of the BN.

fracture toughness of the fused silica were increased by 1.4 and 2.2 times, respectively, with the addition of only 15 vol.% BN. At the optimum composition of 60 vol.% BN, a bending strength of 246 MPa and a fracture toughness of 2.87 MPa·m$^{1/2}$, were achieved, which are 5.2 and 6 times higher than those of the monolithic fused silica, respectively.

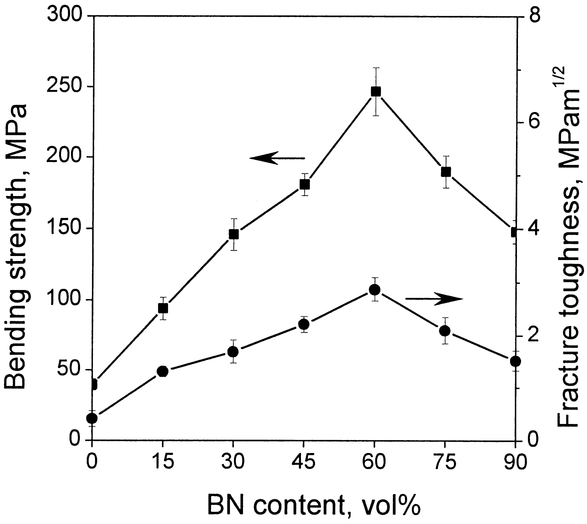

Fig. 3. Variation of bending strength and fracture toughness of the composites with BN content.

Such effective strengthening and toughening effects are attributed to the high relative density of the composites, the desirable interfacial stresses between BN and SiO_2, and the layered crystal structure and the preferential orientation of the flaked BN grains in the composites. At the interface between the BN and the fused silica, the fused silica always suffers from a compressive stress because its coefficient of thermal expansion is slightly lower than that of BN; therefore, it was strengthened by the addition of BN. The typical morphologies of the fracture surface of the composites are shown in Fig. 4. The most evident feature is the pull-out of a large number of BN platelets, with substantial pull-out lengths. A very coarse fracture surface is noted due to very torturous crack propagation paths, which give rise to the relatively high fracture toughness. The preferential orientation of the BN grains (with the planar planes perpendicular to the hot pressing direction) is also evident, which is due to the rotation of the BN flakes during the viscous flow of the fused silica matrix under hot pressing.

The pull-out of the BN flakes is facilitated by its stress state and its platelike morphology. BN has a layered structure similar to graphite, with a strong bonding within each layer and a weak bonding between the layers. In the composites, BN flakes suffered a tensile stress at the BN/SiO_2 interface in both tangential and radial directions. When a crack tip meets a BN grain, it will propagate either along the interface between the fused silica and the BN grains or along the interlayer within the BN grains. Whereas, the crack propagation across a BN flake is difficult because of the strong bonding within each layer of the BN gains. Therefore, the fracture of the composites shows large degrees of crack deflection and pull-out and cleavage cracking of the BN grains.

The cracking paths are also very torturous, as shown by an indentation crack on polished surface in Fig. 5. Moreover, the toughening effects due to the pull-out of BN platelets and to the crack deflection are greatly enhanced by the high relative density of the composites, the coarse and strong bonding between the BN/SiO_2

interfaces, and the preferential orientation of the BN grains. Hence the fracture toughness in the specimen thickness direction (parallel to the direction of hot pressing) is evidently increased.

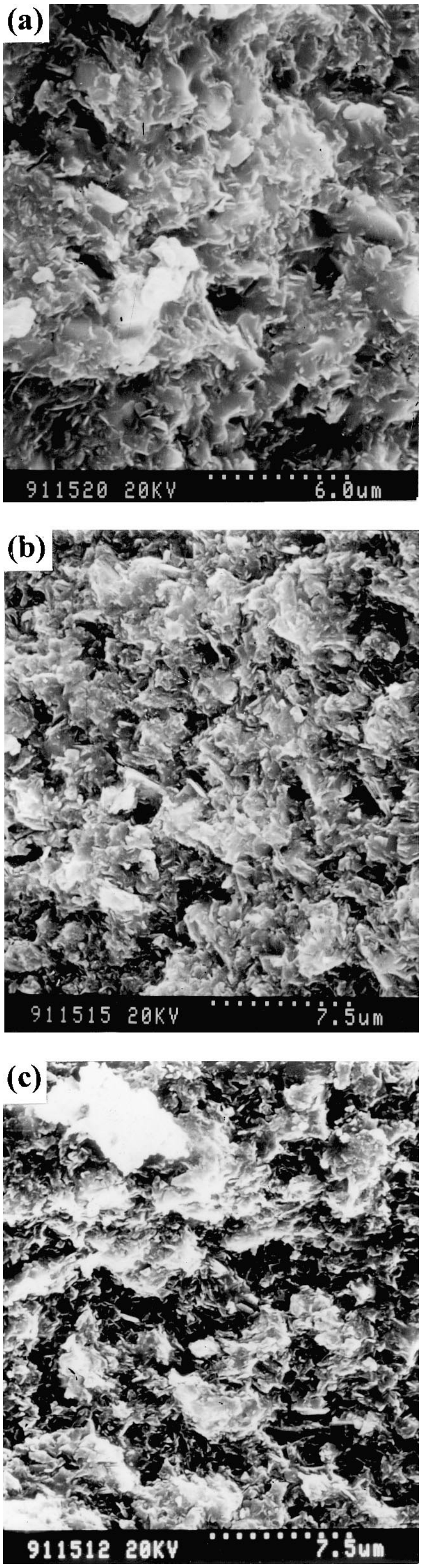

Fig. 4. SEM images showing the morphologies of the fracture surface of the composites, with: (a) 30 vol.% BN, (b) 60 vol.% BN, and (c) 90 vol.% BN.

Fig. 6 shows the variation of the thermal ablation rate with the BN content. It can be seen that the ablation rate decreased with increasing BN content, which is attributed to the high sublimation temperature of the BN. Fig. 7 shows the surface temperature evolution of several composites during the ablation experiment. In all the cases, the surface temperature increases rapidly to a peak value T_p and then drops slightly to a stable value T_s. T_p is of 2500–2850°C, and T_s is in the range of 2150–2450°C. Both T_p and T_s increased with increasing BN content. The presence of T_p is the result of rapid heating of a very thin surface layer that consumed almost all the ablation heat to increase its temperature in a very short period of time. After the initial stage, the surface temperature dropped rapidly, due to heat loss of

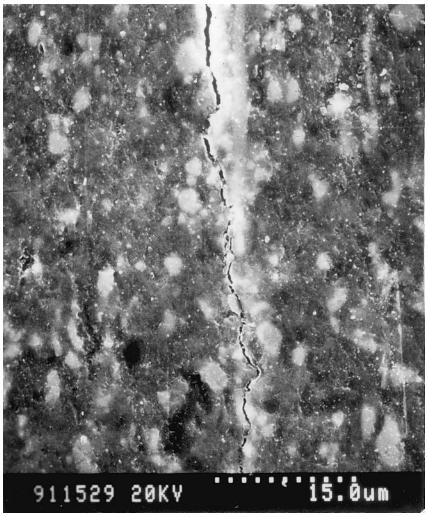

Fig. 5. SEM image showing an indentation crack path on a polished surface of the composite.

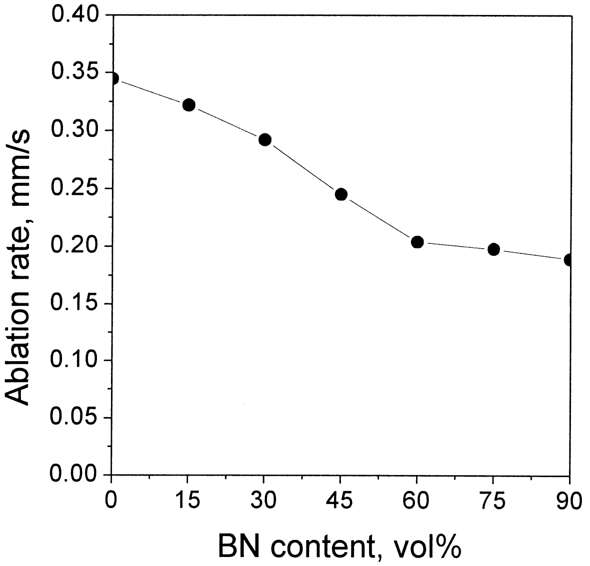

Fig. 6. Variation of the thermal ablation rate of the composites with BN content.

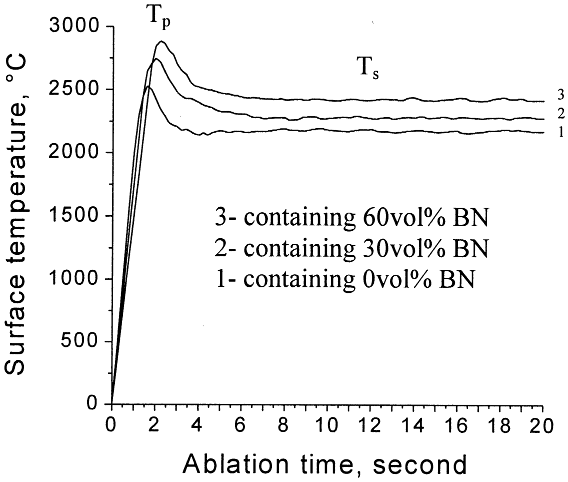

Fig. 7. Ablation surface temperature patterns during ablation.

the sample and to the melting and vaporisation of the fused silica that consumed part of the generated heat. T_s is the equilibrium temperature between heat generation and the total heat loss, including the heats of melting and vaporisation of the fused silica, and the radiation and convection heat loss of the sample itself. With increasing content of the fused silica, the heat loss due to melting and vaporisation increases, which leads to a reduced T_s. For applications that use BN-based materials, a decrease in the ablation surface temperature due to the addition of the fused silica is beneficial to the reduction of signal attenuation.

The surface microstructure of the composites was evidently altered by the ablation. The XRD and FT–IR patterns of the ablated surfaces are shown in Figs. 8 and 9, respectively. It can been seen from the XRD patterns, Figs. 1 and 8, that the intensity of the BN diffraction peak was decreased, whereas the amorphous state of the fused silica almost remained unchanged. On the other hand, two new types of bonds, i.e. of O–B and Si–N, were noted in the ablated materials, as indicated by the FT–IR pattern, Fig. 9. It is suggested from the combination of the two results that BN may be dissolved, at least in part, in the amorphous SiO_2 network at the high ablation temperature, forming a new glass of the Si–B–O–N type. The dissolution of the BN phase certainly increased the viscosity and the softening point of the fused silica. As a result, the denudation of the fused silica (one of the ablation mechanisms for fused silica), and hence the ablation rate of the materials were decreased, as shown in Fig. 6. As a further inference, a Si–B–O–N glass system should be paid particular attention in the development of multi-functional elevated temperature dielectric materials.

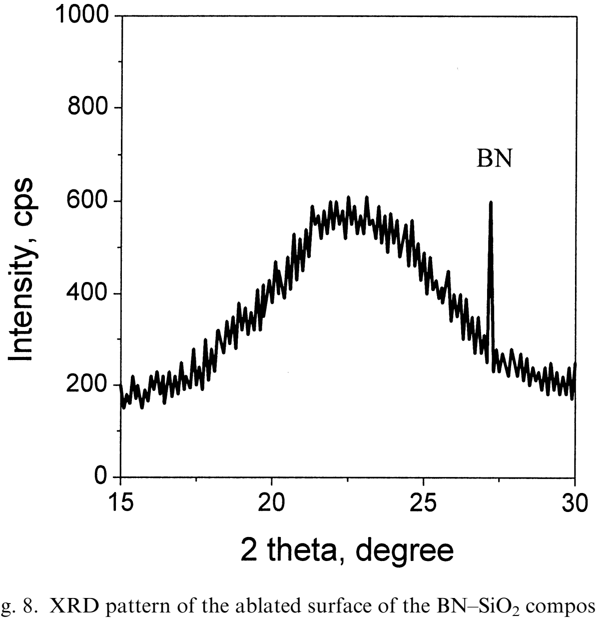

Fig. 8. XRD pattern of the ablated surface of the BN–SiO_2 composite with 30 vol.% BN.

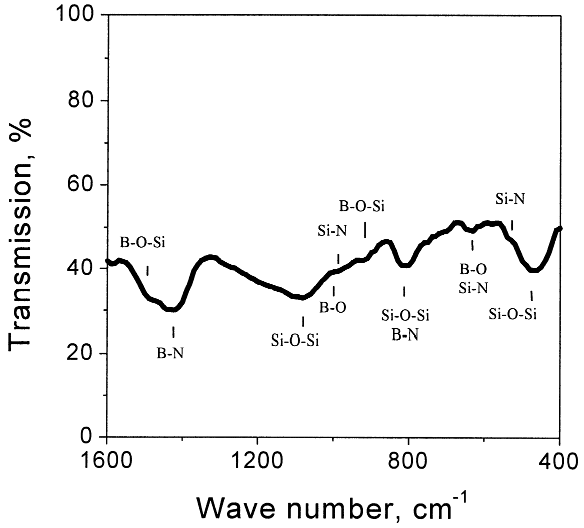

Fig. 9. FT–IR pattern of the ablated surface of the BN–SiO_2 composite with 30 vol.% BN.

4. Summary

A series of BN–SiO_2 composites with high relative densities have been fabricated by hot pressing of a mixture of BN and quartz glass powders. The fused silica and the BN have good chemical and physical compatibilities. In the composites, BN flakes were preferentially orientated by hot pressing and homogeneously distributed in the fused silica continuous matrix. An evident co-operative enhancement has been achieved by the combination of the two constituents. BN materials were modified by the fused silica, with increased sinterability, thermal shock resistance and decreased ablation surface temperature. Whereas, the strength, fracture toughness, and flame ablation resistance of the fused silica were increased by the addition of BN. In addition, an amorphous Si–B–O–N system was identified in the surface layer of the ablated composites, which may be responsible for the much-improved properties of the composites as discussed above. Hence, a new type of Si–B–O–N glass should be paid further attention for applications involving elevated temperature dielectric materials.

Acknowledgements

The authors from HIT would like to thank the support of The Chinese Defence Committee of Technology under the Key National Laboratory Fellowship scheme. The work was completed when GW was a visiting fellow at QMW sponsored by the Royal Society under the FCO Chevening Fellowship scheme.

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