Tuning the electrical, thermal, and mechanical properties of SiC-BN composites using sintering additives

Rohit Malik, Young-Wook Kim, Kwang Joo Kim and B. V. Manoj Kumar

ABSTRACT
SiC-4 vol% BN composites were hot-pressed at 2050°C for 4 h at 40 MPa in a N₂ atmosphere using micron-sized β-SiC and h-BN starting powders with 1 vol% sintering additives. Four batches were prepared using four different types of additive systems, i.e. Y₂O₃-Sc₂O₃, Yb₂O₃-CaO, Yb₂O₃-MgO, and Al₂O₃-AlN-Y₂O₃. The electrical, thermal, and mechanical properties of the SiC-4 vol% BN composites, which are primarily limited by the intrinsic weakness of h-BN and by the point defects (B₁ and A₁) created by the dissolution of B and Al in the SiC lattice, were successfully tuned with the use of different additive systems. The electrical conductivity of SiC-4 vol% BN composites improved fivefold, i.e. from 2.6 (Ω·cm)⁻¹ for the Al₂O₃-AlN-Y₂O₃-containing specimen to 13.9 (Ω·cm)⁻¹ for the Y₂O₃-Sc₂O₃-containing specimen, owing to grain-growth-assisted N-doping and the elimination of Al-derived acceptors. Thermal conductivity was altered by 16% with the use of different additive systems. Fracture toughness dramatically increased from 4.3 MPa·m⁰.⁵ in Yb₂O₃-CaO-containing specimens to 7.3 MPa·m⁻¹ in Y₂O₃-Sc₂O₃-containing specimens. The electrical conductivity, thermal conductivity, flexural strength, and fracture toughness of SiC-4 vol% BN composite sintered with 1 vol% Y₂O₃-Sc₂O₃ were 13.9 (Ω·cm)⁻¹, 82.0 W·m⁻¹·K⁻¹, 505 MPa, and 7.3 MPa·m⁻¹·K⁻¹, respectively.

1. Introduction
Boron nitride (BN)-reinforced silicon carbide (SiC) is an important particulate-reinforced ceramic matrix composite owing to its interesting engineering properties, such as high thermal conductivity, high thermal shock resistance, high-temperature strength, high oxidation resistance, and excellent electrical properties [1–8]. However, there is a lack of extensive research on SiC-BN composites. To date, most of the studies on SiC-BN composites are centered around the effect of the processing route (in-situ/powder-processed) and BN content on the electrical, thermal, and mechanical properties. A brief literature review is as follows: the electrical resistivity of SiC-BN composites could be successfully adjusted in the range of 8.1 × 10⁻³ to 1.0 × 10⁻¹2 Ω·cm by varying the BN content, sintering atmosphere, and processing route. Owing to the more homogeneous distribution of insulating BN throughout the matrix, chemically synthesized SiC-10 vol% BN composite sintered in an Ar atmosphere exhibited higher electrical resistivity (1.0 × 10⁻¹² Ω·cm) [7] than that (9.3 × 10⁻¹³ Ω·cm) [9] reported for the powder-processed composites. The SiC-4 vol% BN composites hot-pressed in a N₂ atmosphere exhibited relatively high electrical conductivity (32.3–123.5 Ω⁻¹·cm⁻¹) due to N-doping into the SiC lattice via solution-reprecipitation during liquid phase sintering (LPS) [10,11]. The hot-pressed SiC-4 vol% BN composite could be successfully electro-discharge machined to intricate shapes [10]. The thermal conductivity of SiC-BN composites varied as 32.2 – 99.7 W·m⁻¹·K⁻¹, decreasing with the addition of the thermally insulating BN phase [9–12]. The chemically processed SiC-BN composites exhibited higher flexural strength than powder-processed composites, attributed to the more homogeneous distribution of BN and grain-refinement facilitated by in-situ synthesized nano-BN present at grain boundaries. The bending strength of chemically processed and powder-processed SiC-BN composites varied as 250–900 MPa and 230–685 MPa, respectively [2,4,6,10,13–16]. In general, the flexural strength decreased with increase in BN content owing to the intrinsic weakness of the BN phase. Compared with the chemically processed composites, powder-processed SiC-BN composites exhibited higher fracture toughness with equivalent BN content owing to the increased crack deflection by the large plate-shaped BN grains. The fracture toughness measured using an indentation method varied as 3 – 4 MPa·m⁰.⁵ and 7 – 9 MPa·m⁰.⁵ for chemically and powder-processed SiC-BN composites, respectively [4,14,16]. Owing to the intrinsic weakness of the BN phase, the hardness of SiC-BN composites deteriorates severely with BN addition [4,6,13,15]. The reported Vickers hardness for chemically processed SiC-BN composites varied as 3.3 – 15.7 GPa as a function of BN content. The powder-processed composites exhibited
similar Vickers hardness values (5.4 – 16.2 GPa) [6,13]. A BN addition of ≥20 vol% results in improved mechanical machinability of SiC-BN composites, attributed to the weak layered structure of BN, which can be easily deformed by the shear force applied by a machining tool [4,6,13,14]. Owing to the large difference in the anisotropic thermal expansion coefficient of BN (α = 40 × 10⁻⁶°C⁻¹ along the c-axis and ≤1 × 10⁻⁶°C⁻¹ perpendicular to the c-axis), large thermal strains developed during cooling are relieved by microcracking, facilitated by the easy cleavage of BN grains perpendicular to the c-axis [1,17]. This microcracking is responsible for the improved thermal shock resistance of SiC-BN composites [14]. In summary, BN addition is beneficial for improving electrical resistivity, fracture toughness, machinability, and thermal shock resistance. However, it significantly deteriorates hardness, thermal conductivity, electrical conductivity, and flexural strength, even at an amount as low as 10 vol%.

To date, there is no study on the effect of sintering additives on the thermal, electrical, and mechanical properties of SiC-BN composites. Several important investigations [18–21] have revealed the importance of sintering additives in determining the electrical, thermal, and mechanical properties of monolithic SiC ceramics. The present work investigates the effect of additive composition and microstructure on the thermal, electrical, and mechanical properties of SiC-4 vol% BN composites. Four additive compositions selected from the previous studies on monolithic SiC and BN are Y₂O₃-Sc₂O₃ [22], Yb₂O₃-MgO [23], Yb₂O₃-CaO [23], and Al₂O₃-AlN-Y₂O₃ [24]. Monolithic SiC exhibited a high thermal conductivity of 262 Wm⁻¹K⁻¹ when sintered with 0.79 vol% Y₂O₃-Sc₂O₃ at 2000°C for 6 h in a N₂ atmosphere [22]. Kusunose et al. [23] reported the highest thermal conductivity (~210 Wm⁻¹K⁻¹) for monolithic h-BN hot-pressed with 15 vol% Yb₂O₃-MgO/CaO at 2000°C for 1 h in a N₂ atmosphere. Similarly, 3 vol% Al₂O₃-AlN-Y₂O₃ additive system exhibited a very high electrical resistivity of ~10¹³ Ωcm for monolithic α-SiC pressureless-sintered at 1900°C for 1 h in Ar [24]. Given that BN addition deteriorates the mechanical properties, and thermal and electrical conductivities, it would be interesting to investigate whether these new additive systems could change these properties. This paper highlights the strategies available to control the electrical, thermal, and mechanical properties of particle-reinforced liquid-phase sintered composites by the judicious selection of sintering additives.

2. Experimental procedure

To prepare SiC-4 vol% BN composites with various additive systems, commercially available β-SiC (~0.5 µm, Grade BF-17, H.C. Starck, Berlin, Germany), h-BN (~10 µm, Grade A01, H.C. Starck, Berlin, Germany), RE₂O₃ (RE = Y, Sc, Yb, 99.99%, Kojundo Chemical Laboratory Co., Ltd., Sakado-shi, Japan), CaCO₃ (99.99%, Kojundo Chemical Laboratory Co., Ltd., Sakado-shi, Japan), MgO (99.99%, Kojundo Chemical Laboratory Co., Ltd., Sakado-shi, Japan), AlN (Grade H, Tokuyama Corp., Tokyo, Japan), and Al₂O₃ (99.999%, AKP-30, Sumitomo Chemical Co., Ltd., Tokyo, Japan) were mixed in the weight ratio shown in Table 1 by ball milling, using SiC balls and a polypropylene jar for 24 h in ethanol. The amount of sintering additive was fixed at 1 vol%, and their relative molar ratios were kept similar to previous studies, i.e., 1:1, 1:1, 1:1, and 1:3:1 for Y₂O₃-Sc₂O₃ [22], Yb₂O₃-MgO [23], Yb₂O₃-CaO [23], and Al₂O₃-AlN-Y₂O₃ [24], respectively. The milled slurry was dried at 60°C overnight, sieved using 60 mesh (250 µm opening), and hot-pressed at 2050°C for 4 h in a N₂ atmosphere under a pressure of 40 MPa.

The details of experimental procedure for sintered density measurement, microstructure observation, crystalline phase analysis using XRD, electrical properties measurement using Hall effect, thermal properties measurement using laser flash method, fracture toughness measurement using ASTM C 1421–15 [25] and flexural strength measurement using ASTM C 1161–13 [26] are described in a previous paper [10].

Grain size measurement was carried out on SEM images using an image analysis software (Image-Pro plus 4.0, Media Cybernetics Inc., MS, USA). In present work, the grain size is defined as the average length of diameters measured at two degrees intervals and passing through the object centroid. At least 700 grains were measured for the statistical analysis of each specimen. The grain size was plotted as a function of areal frequency and the average grain size was taken at one half of the cumulative area. The longest and the shortest diagonal of a grain were designated as its major and minor axis, respectively. The ratio of major to minor axis is defined as the aspect ratio. The mean of the 10% highest observed aspect ratios was taken to be the mean of the actual values (Rₑ). The equation for average phonon mean free path calculation is reported in a previous paper [9,11].

Table 1. Batch composition and relative density of SiC-4 vol% BN composites sintered with various additive systems.

| Sample designation | Batch composition (wt%) | Theoretical density (g/cm³) | Relative density (%) |
|--------------------|-------------------------|----------------------------|---------------------|
| SYSSc              | 95.755% β-SiC + 2.858% BN + 0.861% Y₂O₃ + 0.526% Sc₂O₃ | 3.191 | 98.8 |
| Symb               | 94.683% β-SiC + 2.826% BN + 2.260% Yb₂O₃ + 0.231% MgO | 3.227 | 98.7 |
| SybC               | 94.821% β-SiC + 2.830% BN + 2.057% Yb₂O₃ + 0.292% CaO | 3.222 | 98.9 |
| SAAy               | 95.853% β-SiC + 2.861% BN + 0.644% Y₂O₃ + 0.351% AlN + 0.291% Al₂O₃ | 3.187 | 98.1 |
3. Results and discussion

3.1. Densification, microstructure, and phase analysis

All specimens could be densified to ≥98% of the theoretical density when hot pressed at 2050°C for 4 h in a N₂ atmosphere under a pressure 40 MPa (Table 1). The sintering additives react with the native oxides (SiO₂ and B₂O₃) during sintering, forming a Y/Yb-Sc/Al/Mg/Ca-B-Si-O melt, depending on the additive composition. At high temperature, the oxide melt was transformed to a Y/Yb-Sc/Al/Mg/Ca-B-Si-OCN melt with the dissolution of SiC, BN, and N₂ from the atmosphere. The SiC-BN composites were densified via liquid-phase sintering in the presence of Y/Yb-Sc/Al/Mg/Ca-B-Si-OCN melt. The silica-based melt exhibits different viscosities depending on the modifying elements [27–29], which in turn, determines the diffusion rate of various elements through the melt during sintering and, thus, controls the densification rate. The SAAY specimen sintered with a ternary additive system exhibited the lowest density, which is attributed to the following two reasons: (1) Al forms networks in SiO₂ melt, increasing the viscosity of the liquid melt during sintering and slowing down the densification rate [27,30], and (2) Al dissolves in the SiC lattice [31], reducing the total volume of liquid phase available for liquid-phase sintering. However, basic oxides, such as CaO and MgO [27], and rare earth oxides, such as Y₂O₃ [28] and Yb₂O₃ [29], are reported to reduce the viscosity of SiO₂-based melts. The high density obtained in binary additive systems is attributed to the high densification rate obtained with the less viscous silica-based melt modified with Y, Yb, Ca, Mg, and Sc as opposed to the highly viscous Al-modified silica melt formed in the ternary additive system. The XRD plot and SiC polytypes determined by the Rietveld refinement method for SiC-4 vol% BN composites sintered with various additive systems are shown in Figures 1 and 2, respectively.

As shown in Figure 2, all specimens exhibited the β- to α-phase transformation as BN-derived B is an α-SiC phase stabilizer with finite solubility (2.5 × 10²⁰ cm⁻³) in a SiC lattice [32,33]. In fact, group III elements, including B and Al, are p-type dopants that are known to stabilize hexagonal SiC, whereas n-type dopants, such as N and P, are cubic-phase (β-SiC) stabilizers [34]. Consequently, SAAY exhibited a complete β- to α-phase transformation due to enhanced α-SiC stability in the presence of Al and B, whereas the other three specimens exhibited partial retention of β-SiC in the absence of Al.

The SEM micrographs of SiC-BN composites are shown in Figure 3. All the specimens exhibited predominantly elongated SiC grains, except SAAY, which exhibited a largely equiaxed microstructure. The pore-shaped regions are etched-out BN grains. The important findings from the SEM micrograph are as follows: (1) SYSc (Figure 3(a)) exhibited elongated grains with a high aspect ratio (2.9), implying a preferential grain growth along the c-axis and linear grain boundaries, (2) curved grain boundaries and elongated grains with aspect ratios of 2.5 and 2.4 in SYbM and SYbC, respectively, and (3) predominantly equiaxed grains with a low aspect ratio (1.8) in SAAY. The SAAY specimen exhibited a relatively fine, equiaxed microstructure, attributed to the viscous melt formed during LPS, as discussed before, whereas the other three specimens with a less viscous liquid phase exhibited a relatively coarse microstructure for the same sintering parameters. The equiaxed morphology in SAAY implies that the grain growth is controlled by diffusion, which further confirms the high viscosity of the Y-Al-B-Si-OCN melt [35].

The average grain size, aspect ratio and axis length of SiC grains measured from the SEM images using image analysis software are shown in Figures 4 and 5, respectively. The average grain sizes were 4.9 ± 3.7, 5.4 ± 2.8, 5.1 ± 2.8, and 3.7 ± 1.0 μm for SYSc, SYbM, SYbC, and SAAY, respectively. The SYSc specimen exhibited the highest major axis length (7.5 ± 3.5 μm), followed by
SYbM and SYbC with similar major axis lengths (~6 µm), whereas SAAY specimen with predominantly equiaxed grains exhibited the least major axis length (4.8 ± 2.9 µm). All specimens exhibited a similar minor axis length (2.5 µm).

Figure 6 shows the grain size distribution as a function of area frequency for the SiC-4 vol% BN composites sintered with various additive systems. SYbM, SYbC, and SAAY exhibited an unimodal distribution with a frozen microstructure, whereas SYSc exhibited a wide distribution of grain sizes with a driving force for further coarsening. During LPS, the grain size below a critical size (a function of chemistry and thermodynamics) dissolves in the oxycarbonitride melt and precipitates over large grains via the solution-reprecipitation mechanism. As the critical grain size is a function of melt chemistry, SYSc, with wide distribution of grain size and the highest aspect ratio (Figure 4), exhibits a relatively large critical grain size compared with that of the others. Owing to its large critical grain size, SYSc has high coarsening potential, which is beneficial for achieving grain-growth-assisted high fracture toughness, high thermal conductivity [36], and high electrical conductivity [37]. In summary, the additive systems determine both the kinetics (grain growth rate) and thermodynamics (microstructure) of the ceramic composites. Thus, a judicious selection of additives is crucial for achieving the desired microstructure with required electrical, thermal, and mechanical properties.

3.2. Electrical properties

Figure 7 shows the carrier density and carrier mobility of SiC-4 vol% BN composites sintered with various additive systems, as obtained from the Hall effect measurements.
All specimens were determined to be n-type semiconductors from the Hall effect measurements, attributed to N-doping in a SiC lattice during LPS via solution-reprecipitation. N impurities substitute for C sites (N\textsubscript{C}) to form donor levels near the conduction-band minimum of SiC, dramatically increasing the amount of n-type charge carriers. However, the amount of N-doping in the SiC lattice is a function of (1) the nitrogen solubility in the oxycarbonitride melt, which in turn, depends on the additive composition [21] and (2) the final grain size. A previous study [38] reports a nitrogen solubility of 3.4–3.9% in RE-Si-O-C-N melt (RE = Y, Sc, Lu, Gd, and Sm). Enhanced grain coarsening implies high N-doping during LPS via solution reprecipitation [11]. In the present study, the carrier density followed the trend of the grain size, i.e., SYbM, with the highest grain size (5.4 ± 2.8 µm), exhibited the highest carrier density \(8.0 \times 10^{19} \text{ cm}^{-3}\), and SAAY, with the smallest grain size (3.7 ± 1.0 µm),

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**Figure 6.** Grain size distribution of SiC grains in the SiC-4 vol% BN composites sintered with various additive systems: (a) SYSc, (b) SYbM, (c) SYbC, and (d) SAAY.

**Figure 7.** Plot showing the carrier density and carrier mobility of the SiC-4 vol% BN composites sintered with various additive systems.
exhibited the lowest carrier density \(3.6 \times 10^{19} \text{ cm}^{-3}\). The increase in carrier density with grain size is proportional in the cases of SYbC and SYbM, i.e. for a change of ~6% in grain size, the carrier density increased by ~7%. However, when comparing SYSc with SYbC, the grain size increased only by ~4%, whereas the carrier density increased by ~34%. This implies that an Yb-Mg/Ca-Si-OCN melt has a higher N-solubility than does a Y-Sc-Si-OCN melt. The lowest carrier density exhibited by SAAY is attributed to a small grain size that limited the amount of N-doping via solution-reprecipitation and Al-derived acceptors that compensated for N-derived donors. The newly fabricated SiC-4 vol% BN composites exhibited an order of magnitude lower carrier density than that \((<10^{20} \text{ cm}^{-3})\) reported previously \([10,11]\) for SiC-4 vol% BN composites sintered with 2 vol% \(\text{Y}_2\text{O}_3\). The low carrier density obtained in the present case can be attributed to the lower nitrogen solubility in the Y/Yb-Sc/Al/Mg/Ca-B-Si-OCN melt investigated in the present study compared with the Y-B-Si-OCN melt used in the previous studies \([10,11]\). As shown in Figure 7, SYSc exhibited the highest electrical mobility \((1.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1})\) which is 3 ~ 4 times that of the other additive systems investigated in the present study. Electron mobility is a function of scattering time, i.e., time in which an electron is accelerated before being scattered, which in turn, depends on population density of scattering sites, such as soluble impurities, interfaces, grain boundaries, and defects. Sintering additives play a dominant role in determining the density of scattering sites as evident from the following examples: (1) Al- and B-doped SiC ceramics hot-pressed using Al and B as sintering additives exhibited an order of magnitude higher electrical resistivity \((10^2 \Omega\text{cm, RT})\) than that of undoped SiC, attributed to the annihilation of N-derived donors by Al- and B-derived acceptors \([39]\), and (2) Kim et al. \([24]\) reported a high electrical resistivity of \(~10^{13} \Omega\text{cm}\) for monolithic SiC sintered with 3 vol% \(\text{Al}_2\text{O}_3\)-\(\text{AIN}-\text{Y}_2\text{O}_3\), attributed to the thick amorphous intergranular phase and increased oxygen solubility in the SiC lattice. In the present study, the high and low electron mobility of SYSc and SAAY can be attributed to their low and high scattering site density, respectively. Figure 8 shows a comparison between the electrical resistivity obtained in the present case and the data collected from previous studies on SiC-BN composites. The electrical conductivity for SYSc, SYbM, SYbC, and SAAY were 13.9, 5.0, 4.5, and 2.6 \((\Omega\text{cm})^{-1}\), respectively. In Figure 8, the SiC-BN composites sintered in an Ar atmosphere exhibited higher electrical resistivity \((9.3 \times 10^5 - 1.0 \times 10^{12} \Omega\text{cm})\) \([7,9,12,40]\) than the electrical resistivity \((8.1 \times 10^{-3} - 2.7 \times 10^{-1} \Omega\text{cm})\) obtained in a \(\text{N}_2\) atmosphere \([10,11]\) owing to the formation of N-derived donor levels near the conduction-band minimum of SiC by the doping of nitrogen in the SiC lattice via solution-reprecipitation. In the present study, as a result of low N-solubility, SiC-4 vol% BN composites sintered with 1 vol% of various additives exhibited lower electrical conductivity \((2.6 - 13.9 \Omega\text{cm}^{-1})\) than the electrical conductivity \((32.3 \Omega\text{cm}^{-1})\) reported previously for SiC-4 vol% BN and nano SiC-4 vol% nano-BN composites, respectively \([11]\). Nevertheless, the present study highlights the importance of the additive composition on the electrical properties of composites, such that the electrical conductivity of SiC-4 vol% BN composites could be improved by ~fivefold, i.e. \(2.6 \Omega\text{cm}^{-1}\) in SAAY to \(13.9 \Omega\text{cm}^{-1}\) in SYSc. Based on the aforementioned discussion, we suggest the following strategies in the selection of an additive composition to tune the electrical properties of liquid-phase-sintered SiC-based.
composites: (1) selection of additives promoting grain-growth in a N$_2$ atmosphere to achieve higher carrier densities or additives restricting grain coarsening in an Ar atmosphere to achieve low carrier density, (2) selection of Al- and B-based additives for compensation doping, and (3) selection of additives to minimize lattice defects and produce clean interfaces to achieve higher carrier mobility.

### 3.3. Thermal properties

Figure 9 shows the thermal diffusivity and heat capacity of SiC-4 vol% BN composites sintered with various additive systems. Thermal diffusivity is a material property that determines the rate of heat transfer. Because the heat is primarily conducted via phonons in ceramics, the rate of heat transfer or thermal diffusivity is determined by the amount of phonon scattering, which includes defect-phonon scattering, phonon-grain-boundary scattering, and temperature-activated phonon-phonon scattering. A high density of phonon scattering sites leads to high phonon scattering and deteriorates the thermal diffusivity. In the present study, the thermal diffusivity of SiC-4 vol% BN composites decreased from 35.3 mm$^2$/s to 31.7 mm$^2$/s with a decrease in grain size from 5.4 ± 2.8 µm to 3.7 ± 1.0 µm for SYbM and SAAY, respectively, due to the increased phonon scattering at grain boundaries. Collins et al. [41] reported an increase in thermal diffusivity from 132 mm$^2$/s to 338 mm$^2$/s with an increase in grain size from 6.8 to 17.2 µm for the chemical-vapor-deposited β-SiC, due to the decrease in the phonon-grain boundary scattering with an increase in grain size. The measured heat capacities for SYSc, SYbM, SYbC, and SAAY were 0.742, 0.684, 0.652, and 0.704 J·g$^{-1}$·K$^{-1}$, respectively.

Figure 10 shows the mean free path and thermal conductivity of SiC-4 vol% BN composites sintered with various additive systems. The composites exhibited very low phonon mean free paths (8.6 – 9.4 nm), which are much smaller than those of the average grain size of SiC (3.7 – 5.4 µm), attributed to point defects, i.e. B$_{si}$ and N$_{s}$ created by the dissolution of BN-derived B and N atoms into the SiC lattice, which act as phonon scattering sites [10,11]. In the case of SAAY, additional point defects, such as Al$_{si}$, O$_{s}$, and Si-vacancy, are created by the dissolution of Al into the SiC lattice, which resulted in a further decrease in the phonon mean free path [42]. The experimentally determined solubility limit of B, N, and Al into the SiC lattice at 2200 K are $2.5 \times 10^{20}$, $8 \times 10^{20}$, and $2 \times 10^{21}$ cm$^{-3}$, respectively [43]. Thus, the low thermal diffusivity of SAAY is attributed to both grain refinement and high density of point defects. It should be noted that the thermal conductivity of the newly developed SiC-4 vol% BN composites was predominantly influenced by BN-derived point defects rather than the lattice oxygen. Previous studies [44–46] have established that SiC ceramics do not exhibit any correlation between thermal conductivity and lattice oxygen content when sintered in presence of SiC lattice soluble atoms such as Al and B. For instance, monolithic SiC ceramics [44] sintered with Al$_2$O$_3$–Y$_2$O$_3$–CaO additives exhibited thermal conductivity independent of lattice oxygen content, i.e., 78, 80, and 77 W·m$^{-1}$·K$^{-1}$ with corresponding lattice oxygen content of ~2600, ~3000, and ~3400 ppm, respectively. In another example, Zhou et al. [45] reported a thermal conductivity of 71 W·m$^{-1}$·K$^{-1}$ at 6200 ppm of oxygen content for SiC ceramics sintered with Al$_2$O$_3$–Y$_2$O$_3$ additives, whereas Kim et al. [46] reported a similar thermal conductivity of 68.2 W·m$^{-1}$·K$^{-1}$ at a much lower oxygen content (~2000 ppm) for SiC ceramics sintered with Al$_2$O$_3$–Y$_2$O$_3$–MgO–CaO additive system.

The SYSc specimen, containing high heat capacity, high thermal diffusivity, and high relative density, exhibited the highest thermal conductivity at 82.0 W·m$^{-1}$·K$^{-1}$, whereas SAAY with low thermal diffusivity and low...
sintered density exhibited the lowest thermal conductivity \((70.7 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})\) among the investigated SiC-4 vol% BN composites. The thermal conductivity of \(82.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) obtained for SYSc is quite comparable for an in situ for powder-processed SiC-4 vol% BN composite \([12]\) and lower than \(92.4 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\) for SiC-4 vol% BN composite sintered with 2 vol% \(Y_2O_3\) \([11]\). The present study has presented the importance of sintering additives in controlling the thermal conductivity of SiC-based composites, whereby the thermal conductivity of SiC-4 vol% BN composites could be altered by 16% with the use of different additive systems. Based on the aforementioned discussion, to improve the thermal conductivity of SiC-based composites we propose selecting suitable additives to achieve the following: (1) a coarse microstructure with low grain-boundary-phonon scattering; (2) clean, crystallized, and thinner grain boundaries with reduced interfacial thermal resistance; (3) reduced lattice oxygen and point defects; and (4) avoid the use of additives in the SiC lattice containing soluble elements, such as Al and B.

### 3.4. Mechanical properties

The fracture toughness and flexural strength for SiC-BN composites are shown in Figure 11. The measured fracture toughness values for SYSc, SAAY, SYbM, and SYbC were 7.3 ± 0.2, 7.0 ± 0.2, 4.9 ± 0.1, and 4.3 ± 0.3 MPa m \(^{1/2}\), respectively. SYSc and SAAY exhibited high fracture toughness, attributed to crack deflection along the grain boundaries (Figure 12). The imprints of intergranular fracture are also reflected in the fracture surfaces of SYSc and SAAY, which exhibit a predominantly intergranular fracture, whereas SYbM and SYbC exhibit a predominantly transgranular fracture (Figure 13). Previous studies \([47,48]\) suggest that the chemistry of intergranular film plays a significant role in the crack propagation behavior of liquid-phase-sintered SiC ceramics. The high fracture toughness of SYSc and SAAY can be attributed to the optimal interfacial strength that facilitated intergranular fracture along the grain boundaries. A previous study \([10]\) on powder-processed SiC-BN composites reported a fracture toughness of 3.7 MPa m \(^{1/2}\) for SiC-4 vol% BN composite when sintered with 2 vol% \(Y_2O_3\) and with an average grain size of 3.8 \(\mu\)m. The high fracture toughness obtained in the present case suggests the beneficial effect of present additive systems. The additives form Y-Sc-Si-OCN and Y-A-Si-OCN melts for SYSc and SAAY specimens, respectively, which solidify as intergranular film on grain boundaries and promote intergranular fracture, as evident from Figure 13. Kusunose \([14]\) reported a fracture toughness of \(\sim 4 \text{ MPa} \cdot \text{m}^{1/2}\) for chemically processed SiC-5 – 30 vol% BN sintered with 9 wt% \(Al_2O_3-Y_2O_3\). Kim et al. \([16]\) reported a fracture toughness of \(\sim 7 \text{ MPa} \cdot \text{m}^{1/2}\) for powder-processed SiC-5 vol% BN composite sintered with 10 wt% oxynitride additives. The high fracture toughness shown by powder-processed SiC-BN composites is attributed to the large grain size of BN (\(~ 6 \mu\)m), which is more effective in improving fracture toughness by crack deflection than nano-BN dispersed at the grain boundaries in chemically processed SiC-BN composites. The fracture toughness of 7.3 MPa m \(^{1/2}\) obtained in the present study is the highest ever reported fracture toughness for the SiC-4 vol% BN composites.

As shown in Figure 11, the flexural strength of SiC-4 vol% BN composite varied as 470 – 505 MPa, and SYSc and SAAY exhibited the highest and lowest flexural strength, respectively. The flexural strength of bulk ceramics is determined by the fracture energy, flaw size, and relative density. Given that SYSc, SYbM, and SYbC have comparable grain size and relative density, the high flexural strength of SYSc is attributed to its high fracture energy. The fracture energy calculated using Simpson’s equation \([49]\) by taking 410 GPa (SiC) and 44 GPa (BN) for the elastic modulus, and 0.19 (SiC) and 0.20 (BN) for Poisson’s ratio were 65, 29.3, 22.5, and 59.7 J/m \(^2\) for SYSc, SYbM, SYbC, and SAAY, respectively \([50,51]\). SAAY exhibited the lowest
strength among the investigated compositions, attributed to its low density despite relatively fine microstructure and high fracture energy. The reported flexural strength of SiC-BN composites exhibited a wide variation (249 – 900 MPa), depending upon the processing method, initial BN content, and sintering additive composition [2–4,12–14]. Previous studies on the powder-processed SiC-BN composites exhibited a flexural strength of 567 MPa for SiC-4 vol% BN composite sintered with 2 vol% Y₂O₃ [10], 483 MPa for 5 vol% BN content when sintered with 10 wt% oxynitride glass [16], 554 MPa for SiC-2 vol% BN content without sintering additives [9], 689 MPa for SiC-5 vol% BN sintered with 9 wt% Y₂O₃-Al₂O₃ [14], and 550 MPa for SiC-13.5 vol% BN sintered with 10 wt% Y₂O₃-Al₂O₃ [13]. Previously reported three-point bending strengths for chemically processed SiC-BN...
composites are as follows: 456 MPa for SiC-4.2 vol% BN with 0.6 wt% B, 1.5 wt% C, and 1.5 wt% Al, 618.6 MPa for SiC-13.5 vol% BN with 10 wt% Al₂O₃-Y₂O₃, 765 MPa for SiC-13.5 vol% BN with 10 wt% Al₂O₃-Y₂O₃ [13], 850 MPa for SiC-10 vol% BN with 9 wt% Al₂O₃-Y₂O₃ [14], 765 MPa for SiC-13.5 vol% BN with 10 wt% Al₂O₃-Y₂O₃ [13], and 675 MPa for SiC-5 vol% BN with 10 wt% Al₂O₃-Y₂O₃ [2]. The chemically processed composites exhibited higher flexural strength owing to a more homogeneous distribution of BN than those of powder-processed composites. The flexural strength (470 – 505 MPa) obtained in the present study is 10 – 20% lower than previous values obtained at the equivalent BN content owing to the relatively low density obtained in the present case as a result of the small amount of additives used.

In summary, the present study reveals the role of sintering additives in determining the mechanical properties of SiC-based composites. Fracture toughness could be dramatically increased by ~70% from 4.3 ± 0.3 MPa m¹/² for SYBC to 7.3 ± 0.2 MPa m¹/² for SYSc, attributed to an optimal interfacial energy, which promotes intergranular fracture. The flexural strength could be improved from 470 ± 16 MPa for SAAY to 505 ± 54 MPa for SYSc. The composition of sintering additives controls the density and microstructural parameters, such as grain size, fracture energy, and interfacial energy, which in turn, determines the mechanical properties. Thus, a judicious selection of additives to optimize the aforementioned parameters is a key to achieving high mechanical properties.

4. Conclusions
SiC-4 vol% BN composites were hot-pressed at 2050°C for 4 h in a N₂ atmosphere under a pressure of 40 MPa using four different sintering additive systems, i.e., Y₂O₃-Sc₂O₃, Yb₂O₃-MgO, Yb₂O₃-CaO, and Al₂O₃-AlN-Y₂O₃. The important findings are as follows:

(1) All specimens exhibited ≥98% of the theoretical density. The composite sintered with Y₂O₃-Sc₂O₃ exhibited a coarse microstructure with a wide distribution of grain size, whereas the Yb₂O₃-MgO- and Yb₂O₃-CaO-containing specimens exhibited coarse microstructure with unimodal grain size distribution. However, the relatively fine equiaxed microstructure was obtained for the Al₂O₃-AlN-Y₂O₃-containing specimen, which was attributed to viscous Al-Y-Si-O CN melt, which inhibited grain growth via solution-reprecipitation during LPS.

(2) The electrical conductivity of SiC-4 vol% BN composites could be improved ~fivefold, i.e., 2.6 (Ω·cm)⁻¹ in the Al₂O₃-AlN-Y₂O₃-containing specimen to 13.9 (Ω·cm)⁻¹ in the Y₂O₃-Sc₂O₃-containing specimen due to grain-growth-assisted N-doping and the elimination of Al-derived acceptors.

(3) Thermal conductivity also exhibited variation (70.7 – 82.0 W·m⁻¹·K⁻¹) as a function of the additive composition. SiC-4 vol% BN composite sintered with Al₂O₃-AlN-Y₂O₃ exhibited the lowest thermal conductivity (70.7 W·m⁻¹·K⁻¹) owing to increased grain-boundary-phonon and defect-phonon scattering, attributed to relatively small grain-size and point defects created by Al solubility to the SiC lattice, respectively.

(4) The SiC-4 vol% BN composites sintered with Y₂O₃-Sc₂O₃ exhibited a high fracture toughness of 7.3 ± 0.2 MPa m¹/², which is ~70% higher than the fracture toughness (4.3 ± 0.3 MPa m¹/²) exhibited by the composite sintered with Yb₂O₃-CaO as a sintering additive attributed to the optimal interfacial strength of the Y-Sc-Si-O CN intergranular phase, which promoted intergranular fracture along the grain boundaries. The composites exhibited variable flexural strength (470 – 505 MPa), attributed to the different values of fracture energy, grain size, and density obtained with different additives.

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ORCID
Rohit Malik http://orcid.org/0000-0001-8764-3321
Young-Wook Kim http://orcid.org/0000-0001-6275-0323
B. V. Manoj Kumar http://orcid.org/0000-0003-1165-423X

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