Effect of additive content on the mechanical and thermal properties of pressureless liquid-phase sintered SiC

Rohit Malik, Yong-Hyeon Kim and Young-Wook Kim

Functional Ceramics Laboratory, Department of Materials Science and Engineering, The University of Seoul, Seoul, Republic of Korea

ABSTRACT
Pressureless liquid-phase sintered SiC (LPS-SiC) ceramics fabricated from β-SiC and 1 vol% α-SiC seeds with 3–15 vol% Al₂O₃-Y₂O₃-CaO additives were prepared to investigate the effects of additive content on the mechanical and thermal properties. All the specimens consisted primarily of elongated α-SiC grains that were predominantly formed via β to α phase transformation and via the growth of the initially added α-SiC seeds during the sintering. The grain growth and polytypic transformation exhibited diffusion-controlled kinetics. The highest value for fracture toughness (5.4 MPa·m⁰.⁵) was exhibited at an additive content level of 7 vol%; this was attributable to the optimal interfacial strength and well-interlocked elongated grains with active crack-microstructure interaction. The specimen with 7 vol% additive content exhibited the highest flexural strength (686 MPa) among the reported pressureless LPS-SiC ceramics, and this was attributable to its high density and the optimal content of soft intergranular phase (IGP). The hardness and thermal conductivity decreased gradually with the increase in additive content, owing to the increased volume fraction of the soft IGP with low thermal conductivity.

1. Introduction

The liquid phase sintering (LPS) technique has made it possible to densify SiC ceramics at a temperature as low as 1750°C, though those could otherwise only be sintered at temperatures above 2000°C via solid-state sintering [1–7]. During LPS, sintering additives react with the native SiO₂ (present on the SiC particle surface) and form a low-temperature silica-based melt (from 1170°C for Al₂O₃–CaO–SiO₂ to 1680°C for the Er₂O₃–SiO₂ eutectic composition), which is responsible for the densification of SiC ceramics at low temperatures (1750–2000°C) via the solution-reprecipitation mechanism [2–4,7,8]. The LPS process is controlled by (1) sintering additive chemistry and (2) sintering additive content.

Thus far, extensive research has been conducted on the effect of additive chemistry on microstructure and the various properties of the SiC ceramics. In fact, the microstructure and mechanical, thermal, and electrical properties of the SiC ceramics can be tuned by adjusting the chemistry of the sintering additives [2,9–15]. For example, SiC ceramics exhibited a high fracture toughness (8.4 MPa·m¹/²) when sintered with Al₂O₃-Y₂O₃-CaO [10], high flexural strength (1077 GPa) when sintered with Y₂O₃–Sc₂O₃–MgO [11], high thermal conductivity (262 Wm⁻¹K⁻¹) when sintered with Y₂O₃–Sc₂O₃ [12], high electrical conductivity (6.7 × 10⁸ Ω⁻¹cm⁻¹) when sintered with Y₂O₃–Lu₂O₃ [13], high electrical resistivity (~10¹³ Ω cm) when sintered with Al₂O₃–AlN–Y₂O₃ [14], and high flexural strength (~600 MPa) at an elevated temperature (1600°C) when sintered with AlN–Lu₂O₃ [15].

However, there are few studies [16–21] that have focused on the effect of the sintering additive content in LPS-SiC ceramics. The literature reveals that the sintering additive content plays a vital role in determining the densification behavior and structural properties of the LPS-SiC ceramics and SiC-based composites [16–21]. For example, SiC–50 wt% Si₃N₄ composites hot pressed with oxynitride composition (5–20 wt%) exhibited: (1) a gradual increase in the sintered density until saturation at 15 wt% additive content, (2) an improvement in flexural strength with up to 15 wt% additive content, and then a decrease in flexural strength at 20 wt% additive content owing to the increased volume fraction of a relatively weak intergranular phase (IGP), and (3) a gradual increase in fracture toughness with the additive content, which can be attributed to the increased accularity of grains at the high additive content [17]. Similarly, the SiC–TiB₂ composites hot pressed with SiO₂–Y₂O₃ (5–20 wt%) exhibited a gradual increase in the sintered density (97.3–98.1%) and fracture toughness (5.7–7.1 MPa m¹/²) with an increase in the additive content, which can be attributed to the enhanced densification and coarse microstructure with weak interfaces, respectively, that occur at a high level of the additive content [18].

CONTACT Young-Wook Kim ywkim@uos.ac.kr
Department of Materials Science and Engineering, The University of Seoul, Seoul 02504, Republic of Korea

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In general, the hot-pressed LPS-SiC ceramics exhibited improved densification and increased fracture toughness at a high level of additive content [17,18]. In the case of pressureless LPS-SiC, the literature presents contradicting results and the effect of additive content remains unclear. For example, in one case, Gubernat et al. [20] reported pressureless LPS-SiC with Al$_2$O$_3$-Y$_2$O$_3$ (5–20 wt%) that exhibited a constant density (~95%), a gradual increase in flexural strength (332–498 MPa), and a gradual decrease in hardness with the increase in additive content, whereas the highest fracture toughness (5.9 MPa m$^{1/2}$) was obtained at 10 wt% additive content. Comparatively, in another report [21], pressureless LPS-SiC ceramics with Al$_2$O$_3$-Y$_2$O$_3$ (5–25 wt%) additives exhibited: (1) an improvement in sintered density up to 10 wt% additive content, and a gradual decrease thereafter, with an increase in the additive content; this can be attributed to the deleterious reaction between SiC and additives causing porosity with the escape of gaseous species (SiO, Al$_2$O, and CO), and (2) a gradual decrease in flexural strength and hardness with an increase in additive content. Thus, the effect of sintering additive content in pressureless LPS-SiC is still not well understood and must be investigated. The economic competitiveness of pressureless LPS-SiC for industrial application is determined by the judicious selection of optimal additive content because rare earth (RE)-based sintering additives are far more expensive than SiC powder.

A previous study [22] reported high density (99.0%) and high flexural strength (628 MPa) for pressureless LPS-SiC ceramics with 7 vol% Al$_2$O$_3$-Y$_2$O$_3$-CaO sintered at 1850°C for 2 h in an Ar atmosphere. The Al$_2$O$_3$-Y$_2$O$_3$-CaO additive system provided high density (>97%) at a relatively low temperature (1800°C), attributed to (1) the low melting temperature of the Al$_2$O$_3$-Y$_2$O$_3$-CaO-SiO$_2$ quaternary system, and (2) the reduced evaporative loss and retarded deleterious reaction between SiC and sintering additives at a low sintering temperature (<1900°C). The present study investigates the effects of the additive content on the mechanical and thermal properties of a pressureless LPS-SiC (β-SiC + 1 vol% α-SiC) with (3–15 vol%) Al$_2$O$_3$-Y$_2$O$_3$-CaO additives.

### Table 1. Batch composition, bulk density, and residual porosity of pressureless LPS-SiC ceramics with Al$_2$O$_3$-Y$_2$O$_3$-CaO additives sintered at 1850°C for 2 h in an argon atmosphere.

| Sample | Batch composition (wt%) | Bulk density (g/cm$^3$) | Residual porosity (%) |
|--------|--------------------------|--------------------------|-----------------------|
| SC3    | 92.55% β-SiC + 0.94% α-SiC + 2.49% SiO$_2$ + 2.38% Al$_2$O$_3$ + 1.32% Y$_2$O$_3$ + 0.32% CaCO$_3$ | 3.08 | 2.61 |
| SC7    | 87.50% β-SiC + 0.89% α-SiC + 2.36% SiO$_2$ + 5.48% Al$_2$O$_3$ + 3.03% Y$_2$O$_3$ + 0.74% CaCO$_3$ | 3.12 | 0.37 |
| SC10   | 83.81% β-SiC + 0.85% α-SiC + 2.26% SiO$_2$ + 7.74% Al$_2$O$_3$ + 4.29% Y$_2$O$_3$ + 1.05% CaCO$_3$ | 3.13 | 0.14 |
| SC15   | 77.48% β-SiC + 0.78% α-SiC + 2.08% SiO$_2$ + 11.81% Al$_2$O$_3$ + 6.29% Y$_2$O$_3$ + 1.56% CaCO$_3$ | 3.15 | 0.19 |

2. **Experimental procedure**

The SiC ceramics were prepared from commercially available β-SiC (~0.5 μm, Grade BF-17, H.C. Starck, Berlin, Germany), α-SiC (A-1 grade, 0.45 μm, H.C. Starck, Berlin, Germany), Y$_2$O$_3$ (99.99%, Kojundo Chemical Laboratory Co., Ltd., Sakado-shi, Japan), CaCO$_3$ (99.99%, Kojundo Chemical Laboratory Co., Ltd., Sakado-shi, Japan), and Al$_2$O$_3$ (99.99%, AKP-30, Sumitomo Chemical Co., Ltd., Tokyo, Japan) as starting materials. CaCO$_3$ was used as the source of CaO. The manufacturer’s data gives an oxygen content of 1.4 and 1.0 wt% for β-SiC and α-SiC powders, respectively. It was assumed that the oxygen was present as native silica in the raw powders. The raw materials were measured according to the weight percentage shown in Table 1, and subsequently ball milled in a polypropylene jar using SiC balls for 24 h in ethanol. The milled slurry was dried and subsequently pressed into a rectangular hexahedron (40 mm × 40 mm × 5 mm) at 50 MPa after sieving (60 mesh), followed by isostatic pressing at 275 MPa.

The green pellets were placed in a graphite crucible containing SiC-Al$_2$O$_3$-Y$_2$O$_3$-CaO bedding powders and sintered at 1850°C for 2 h in an argon atmosphere without applied pressure. The Archimedes method was used to measure the bulk density and residual porosity of the sintered pellets after cutting and polishing. The details of the experimental procedure for crystalline phase analysis using XRD, microstructure observation using SEM, flexural strength measurement using ASTM C1161-13 [23], and fracture toughness measurement using ASTM C1421-18 [24] have been reported in previous papers [22, 25–28]. 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 ratio of longest to shortest diagonal 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 (R$_{50}$).

The thermal diffusivity (α) and heat capacity (C$_p$) were measured using the laser flash technique (Model LFA 467, NETSCH GmbH, Selb, Germany) after applying a thin graphite coating over the samples.
(10 mm x 10 mm x 2 mm). The laser flash system was calibrated using a reference sample (Pyroceram 9606, NETSCH GmbH, Selb, Germany) with known specific heat capacity. Each specimen was measured three times in an argon atmosphere and the thermal conductivity (κ) was calculated using the equation \( \kappa = \alpha \rho C_p \), where \( \rho \) denotes the bulk density of the specimen.

3. Results and discussion

3.1. Densification, phase analysis, and microstructure

The SiC ceramics exhibited a residual porosity of \( \lesssim 2.61\% \) when sintered with Al\(_2\)O\(_3\)-Y\(_2\)O\(_3\)-CaO additives (3–15 vol\%) without applied pressure for 2 h in an argon atmosphere (Table 1). During the sintering, the oxide additives reacted with the native SiO\(_2\) to form an Al-Y-Ca-Si-O melt that transformed into an Al-Y-Ca-Si-O-C melt at high temperatures with the dissolution of SiC [22,29–31]. The Al-Y-Ca-Si-O-C melt was responsible for the densification of the SiC ceramics via the solution-reprecipitation mechanism. Due to the unavailability of the quaternary phase diagram, it is difficult to determine the exact melt formation temperature for each specimen. However, from the ternary phase diagrams of SiO\(_2\)-CaO-Al\(_2\)O\(_3\) and SiO\(_2\)-Y\(_2\)O\(_3\)-Al\(_2\)O\(_3\) [32,33], an increase in liquid formation temperature is expected with a decrease in silica content from 2.49wt\% in SC3 to 2.08wt\% in SC15. Literature reveals that the viscosity of aluminosilicate glasses decreases rapidly as the temperature rises and very low viscosities are asymptotically reached at higher temperatures (\( >1700^\circ\mathrm{C} \)) [34]. Thus, at the sintering temperature (1850°C) used in the present study, one can expect very little change in diffusivities with the variation in SiO\(_2\) content.

The porosity decreased from 2.61 (SC3) to 0.37\% (SC7) with an increase in additive content from 3 to 7 vol\% owing to the increased mass diffusion at a high level of additive content. However, with a further increase in the additive content, the beneficial effect of increased mass diffusion was mitigated by increased diffusion distance and evaporative loss of the additive at a high level of additive content. The measured weight loss during the sintering increased with the increase in the additive content, i.e., 5.2, 8.4, 11.4, and 15.5 wt\% for SC3, SC7, SC10, and SC15, respectively. Previous studies [7,21,22] reported a weight loss for the pressureless LPS-SiC ceramics attributed to (1) the partial evaporation of the sintering additives, and (2) the reaction between Al\(_2\)O\(_3\) and SiC which produces volatile species such as Al\(_2\)O and SiO at \( \gtrsim 1900^\circ\mathrm{C} \). Given that the sintering was performed at 1850°C, the weight loss is primarily attributed to the evaporative loss of additives in the present case. The high densification obtained in the newly developed LPS-SiC ceramics was also attributed to the beneficial effect of an addition of 1 vol\% α-SiC seed. The literature [25] reveals that α-SiC seeds added to β-SiC ceramics promote grain refinement and densification. In the absence of α-SiC seeds, β-SiC particles exhibit high grain coarsening accelerated by β to α phase transformation during the sintering. The in-situ formed α-SiC platelets prefer to grow along the c-axis, impinging against each other and hindering the elimination of residual pores by grain shape accommodation [35,36]. However, the added α-SiC seeds impede the growth of in-situ formed α-SiC platelets, leading to a more equiaxed microstructure that facilitates the removal of residual pores by grain shape accommodation.

Figure 1 and Table 2 show the XRD plots and polytype contents in pressureless sintered LPS-SiC ceramics with Al\(_2\)O\(_3\)-Y\(_2\)O\(_3\)-CaO. As shown in Figure 1, the SiC peak intensity decreased with the increase in additive content.

### Table 2. Polytype contents in pressureless LPS-SiC ceramics with Al\(_2\)O\(_3\)-Y\(_2\)O\(_3\)-CaO additives sintered at 1850°C for 2 h in an argon atmosphere. The polytype content was determined using the Rietveld analysis method.

| Sample | 3C-SiC | 6H-SiC | 4H-SiC | Y\(_2\)Al\(_3\)AlO\(_6\) |
|--------|--------|--------|--------|------------------|
| SC3    | 4.3    | 56.8   | 38.9   | –                |
| SC7    | 6.7    | 49.7   | 43.0   | 0.6              |
| SC10   | 8.6    | 38.1   | 49.7   | 3.6              |
| SC15   | 10.0   | 34.2   | 47.7   | 8.1              |
due to the reduced volume fraction of SiC. Several new peaks were detected in the sintered specimen due to the partial crystallization of liquid phase, forming $Y_2Al_2(AlO_3)_3$ phase (JCPDS No. 82–0575) through the reaction between $Y_2O_3$ and $Al_2O_3$ [22]. The relevant findings from the Rietveld analysis (Table 2) are: (1) predominant $\beta$ to $\alpha$ phase transformation took place at a low temperature of 1850°C, attributed to the low melting point of the $Al_2O_3-Y_2O_3-CaO$ quaternary system. (2) The decrease in grain size with an increase in additive content implies that grain growth is diffusion-controlled in the present case. For diffusion-controlled grain-growth kinetics, the grain size decreases with an increase in the additive content because of increased diffusion distance through the liquid [39,40]. As shown in Figure 3(a), the aspect ratio (~4.4) did not exhibit any dependence on the amount of liquid phase. However, the longest diagonal decreased from 3.0 $\mu$m for SC3 to 2.3 $\mu$m for SC15 and the corresponding decrease in the shortest diagonal was 0.7 to 0.5 $\mu$m (Figure 3(b)). The decrease in the length of the grain diagonal at high additive content also confirms the diffusion-controlled kinetics of grain-growth in the present case. The insensitivity of aspect ratio to additive content implies that the relative growth rate of basal to prism planes of $\alpha$-SiC platelet is a function of additive chemistry rather than the additive content in the present case.

Figure 4 shows the grain size distribution of pressureless LPS-SiC with $Al_2O_3-Y_2O_3-CaO$ additives. The SiC ceramics exhibited a bimodal grain size distribution: (1) the first peak at approximately ~1 $\mu$m resulted from equiaxed and small elongated grains, and (2) the second peak at approximately ~2 $\mu$m resulted from the growth of initially added $\alpha$-SiC seeds during sintering. The first peak was clearly visible in all the specimens; however, the intensity of the second peak decreased with the increase in additive content because of the restricted diffusion-controlled grain growth of $\alpha$-SiC seeds at a high level of additive content. In summary, optimal additive content is crucial for...
obtaining high density and the desired microstructure in pressureless LPS-SiC. A low additive content causes poor densification, which is attributed to an insufficient amount of liquid phase. However, a higher level of additive content than the optimum is also disadvantageous in two ways: (1) it hinders the diffusion-controlled grain coarsening which is essential to tune the grain-growth-controlled thermal and electrical conductivity [26,41], and (2) it causes high evaporative loss of expensive additives.

3.2. Mechanical properties

The fracture toughness and flexural strength as a function of additive content of pressureless LPS-SiC with \( \text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3\cdot\text{CaO} \) additives are shown in Figure 5. The SEM images of crack propagation induced by a Vickers indentation and the typical fracture surfaces of pressureless LPS-SiC ceramics are shown in Figures 6 and 7, respectively. The fracture toughness increased from 4.9 MPa-m\(^{1/2} \) for SC3 to 5.4 MPa-m\(^{1/2} \) for SC7, and thereafter it decreased with an increase in additive content. The crack propagation behavior (Figure 6) revealed crack deflection along the grain boundaries to be the dominant mechanism controlling fracture toughness in the present case. In Figure 7, the fracture surface of the pressureless-sintered SiC ceramics revealed an increased tendency toward intergranular fracture with an increase in additive content, owing to an increased volume fraction of intrinsically weak IGP at a high level of additive content. Due to the unavailability of data on the Al-Y-Ca-Si-O-C melt, the physical properties of IGP are unknown. Literature [42–44] reveals that the elastic modulus of the aluminosilicate glasses modified with \( \text{Y}_2\text{O}_3 \) and CaO varies as 90–135 GPa and decreases with an increase in the silica content.

The two important prerequisites for improving fracture toughness by crack deflection are (1) elongated grains with a high aspect ratio, and (2) optimal interfacial strength causing intergranular fracture with active crack-microstructure interaction [10,37]. The low fracture toughness obtained for SC3 was attributed to the insufficient amount of IGP, which failed to cause predominant intergranular fracture (Figure 7(a)), resulting in poor microstructure-crack interaction (Figure 6(a)), whereas the reduced fracture toughness of SC10 and SC15 was possibly attributed to larger volume fraction of IGP than optimum, which reduced the interlocking of SiC grains and thus facilitated easy cleavage along the IGP or IGP-SiC grain interfaces with poor microstructure-crack interaction (Figure 6(c,d)). In the case of an intergranular fracture, the crack can either propagate through the IGP or along the interface between the SiC grain and IGP [45–47]. The choice of preferred crack path depends on the chemical composition of the IGP and the atomic structure of the grain/IGP interface [45,46]. It is practically difficult to determine the preferred crack path even using a sophisticated in-situ TEM investigation because the reliability of data obtained from a limited number of HRTEM images remains questionable [45–47]. A reliable interpretation of the preferred crack path requires the first-principles calculations coupled with HRTEM analysis [47]. The high fracture toughness obtained for SC7 was attributed to the well-interlocked, elongated SiC grains and optimal interfacial strength, which provided increased crack deflection with its active microstructure-crack interaction (Figure 6(b)). The fracture toughness value of 5.4 MPa-m\(^{1/2} \) obtained for the present case was comparable to the fracture toughness (5.3 MPa-m\(^{1/2} \)) reported previously for SiC ceramics with 7 vol% \( \text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3\cdot\text{CaO} \) additives pressureless sintered at 1850°C for 2 h in an argon atmosphere [22]. The fracture toughness determined using the surface crack in flexure method for the present study was lower than the fracture toughness (6–8 MPa-m\(^{1/2} \)) estimated from the Vickers indentation method in the literature [16,48,49] for a similar microstructure. The fracture toughness value determined by the surface crack in flexure method is 1–2 MPa-m\(^{1/2} \).
lower than the one estimated using the Vickers indentation method.

As shown in Figure 5, the flexural strength increased from 642 MPa for SC3 to 686 MPa for SC7, and thereafter it decreased rapidly with an increase in additive content, i.e., 618 and 479 MPa for SC10 and SC15, respectively. The flexural strength of sintered SiC ceramics depends on grain size, volume fraction of liquid phase, and processing defects such as pores [50,51]. The critical flaw sizes (c) were calculated from the measured flexural strength (σ) and fracture toughness (KIC) using the equation $K_{IC} = 1.35\sigma c^{1/2}$, assuming a semielliptical flaw. The calculated critical flaw sizes for SC3, SC7, SC10, and SC15 were 32, 34, 33, and 48 µm, respectively. As the critical flaw size is an order of magnitude greater than the average grain size of SiC (1.2–1.8 µm), the fracture must have originated from the processing defects in the present case rather than the grains. Thus, grain size is not an important factor controlling strength in the present case. Figure 8 shows typical fracture origins for SC7 and SC15, which were residual pores. The decrease of flexural strength from 686 MPa to 479 MPa with increasing additive content from 7 vol% to 15 vol% was attributed to the increased defect size (pore size, refer to Figure 8) and partly large volume fraction of IGP. Thus, the variation of flexural strength in pressureless LPS-SiC ceramics sintered with variable additive content can be explained as a combined effect of the critical defect size (pore size) and the volume fraction of intrinsically weak IGP.

Figure 9 shows a comparative plot of flexural strength as a function of sintering temperature for the pressureless LPS-SiC ceramics fabricated in the present study compared with values from the literature [7,22,25,27,52–59]. The literature for pressureless sintered SiC reports a wide variation in flexural strength (321–634 MPa) depending on the additive content, additive chemistry, and sintering temperature. In Figure 9, pressureless LPS-SiC ceramics sintered using binary additive systems are depicted by solid symbols, whereas those sintered using ternary and quaternary additive systems are depicted by partially shaded and hollow symbols, respectively. Figure 9 reveals a decrease in sintering temperature with the change in the additive system from binary to
quaternary, attributed to the low eutectic temperature of a multi-component additive system \[7,22,27\]. Liang et al. \[54\] densified SiC ceramics to > 99% of the theoretical density using Al\(_2\)O\(_3\)-CeO\(_2\) at a low temperature of 1840°C without applied pressure and reported a three-point bending strength of 437 MPa. Among the investigations on pressureless sintering of SiC using Al\(_2\)O\(_3\)-Y\(_2\)O\(_3\) as an additive system \[20,37,53–56,59\], Magnani et al. \[53\] reported a density of 97.1% at 1875°C with a four-point bending strength of 532 MPa, and She and Ueno \[59\] reported a relative density of 98.1% for pressureless LPS-SiC, sintered at 1950°C with a three-point bending strength of 625 MPa. Using a ternary additive system (7 vol%, Al\(_2\)O\(_3\)-Y\(_2\)O\(_3\)-CaO), Eom et al. \[22\] reported a relative density of 98.1% for liquid-phase SiC pressureless sintered at 1800°C with a four-point flexural strength of 634 MPa. The high density obtained with a ternary system was attributed to the low sintering temperature, which prevented deleterious reactions between alumina and SiC and reduced the evaporative loss of oxide additives. The present study exhibited the highest-ever
reported flexural strength for pressureless sintered SiC, i.e. 686 MPa for SC7, which was attributed to the reduced grain size (1.6 μm) and increased sintered density with the addition of 1 vol% α-SiC, whereas the previous work [22] exhibited a flexural strength of 628 MPa with an average grain size of 1.8 μm and a density of 99.0% for pressureless LPS-SiC ceramics with 7 vol% of Al₂O₃-Y₂O₃-CaO sintered at 1850°C for 2 h in an argon atmosphere. Previous studies [25,37] have reported an improvement in density, flexural strength, and grain refinement for pressureless LPS-SiC ceramics fabricated from β-SiC starting powders containing 1–3 vol% of α-SiC.

The hardness of pressureless LPS-SiC ceramics with Al₂O₃-Y₂O₃-CaO additives is shown in Figure 10. The hardness gradually decreased from 27.0 GPa for SC3 to 20.8 GPa for SC15. The reported value of the Vickers hardness for the pressureless sintered SiC ceramics varied from 22 to 30 GPa depending on the microstructure, residual porosity, and composition [5,7,14,22,52,60–62]. The decrease in hardness with an increase in additive content from 3 vol% in SC3 to 7 vol% in SC7, in spite of the lower residual porosity and smaller grain size of the latter than the former, implies that hardness is predominantly affected by the amount of amorphous IGP in the present case. These results are consistent with previous findings that a high level of additive content is detrimental to hardness [59,60].

### 3.3. Thermal properties

The thermal properties of pressureless LPS-SiC ceramics with Al₂O₃-Y₂O₃-CaO additives are shown in Figures 11 and 12. As shown in Figure 11, the thermal diffusivity decreased gradually from 32.7 mm²/s for SC3 to 28.1 mm²/s for SC15, attributed to (1) the increased volume fraction of predominantly amorphous IGP with low thermal diffusivity, (2) the increased phonon–grain boundary scattering with reduced grain size at a high level of additive content, and (3) increased phonon-heterophase (SiC-IGP) scattering at a high level of additive content. The thermal diffusivity (28.1–32.7 mm²/s) obtained in the present case is comparable with the thermal diffusivity (23.7–33.9 mm²/s) of the pressureless LPS-SiC ceramics with 7 vol% of Al₂O₃-Y₂O₃-CaO [22] and 7 vol% of Al₂O₃-Y₂O₃-CaO-MgO [7], which exhibited a high density (> 97%) and an average grain size of 0.6–2.4 μm when sintered at 1750–1900°C in an argon atmosphere. The literature [7,12,13,22] reveals that the thermal diffusivity (23.7–33.9 mm²/s) of SiC ceramics sintered using Al-based additives is much lower than the thermal diffusivity (80.9–111.6 mm²/s) of those sintered without an Al-based additive. The dissolution of Al in the SiC lattice creates point defects (Al⁺, O₃⁻, V₅⁺) that act as phonon scattering sites and lower the thermal diffusivity [22,28,63,64].

In Figure 11, the specific heat capacity exhibits a small change (~3%) with the change in additive content. Specific heat capacity depends on composition and degree of crystallinity. The specific heat capacities of SiC, Al₂O₃, Y₂O₃, and CaO are 0.678, 0.753, 0.448, and 0.753 Jg⁻¹ K⁻¹, respectively [65]. The specific heat capacity of the IGP estimated using the rule of mixtures is 0.603 Jg⁻¹ K⁻¹. Thus, the marginal decrease in specific heat capacity with an increase in additive
content is attributed to the low specific heat capacity of the IGP.

As shown in Figure 12, the thermal conductivity exhibited a gradual decrease from 71.7 W·m⁻¹·K⁻¹ in SC3 to 62.6 W·m⁻¹·K⁻¹ in SC15. Thermal conductivity is a product of density, thermal diffusivity, and specific heat capacity. Due to its high specific heat capacity and thermal diffusivity, SC3 exhibited marginally higher thermal conductivity than SC7 despite its higher residual porosity (2.61%). The decrease in specific heat and thermal diffusivity for additive content exceeding 7 vol% resulted in poor thermal conductivity. In summary, a high additive content deteriorates the thermal performance of SiC ceramics by increasing the phonon scattering sites, i.e. by increasing the heterogeneous grain boundaries, pore interfaces, and increased grain boundaries per unit volume at a high level of additive content [66,67]. The reported thermal conductivity of pressureless LPS-SiC varied from 55 to 110 W·m⁻¹·K⁻¹ as a function of additive chemistry and microstructure [14,22,27,68,69]. For example, pressureless LPS-SiC ceramics exhibited a thermal conductivity of 55–70 W·m⁻¹·K⁻¹ for 10 vol% Al₂O₃-Y₂O₃ [68], 55–80 W·m⁻¹·K⁻¹ for 9 wt% Al₂O₃-Y₂O₃-CaO [22], 81 W·m⁻¹·K⁻¹ for 3 vol% Al₂O₃-Y₂O₃-AlN [14], 61–82 W·m⁻¹·K⁻¹ for 9 wt% Al₂O₃-Y₂O₃-SrO-CaO [27], 92–110 W·m⁻¹·K⁻¹ for 6.5 vol% Y₂O₃-Sc₂O₃-AlN [69] and 52.8–83.2 W·m⁻¹·K⁻¹ for 9 wt% Al₂O₃-Y₂O₃-MgO-CaO [7].

In spite of a high additive content (~19 wt%), the thermal conductivity (62.6 W·m⁻¹·K⁻¹) of SC15 was within the range found in the literature (55–84 W·m⁻¹·K⁻¹ for Al₂O₃-based additives), implying that the thermal conductivity of SiC ceramics sintered using Al-based additives is more influenced by phonon–point defect scattering rather than the level of additive content.

4. Conclusions

Four SiC ceramics were prepared from β-SiC and α-SiC (1 vol%) starting powders using 3, 7, 10, and 15 vol% of Al₂O₃-Y₂O₃-CaO as a sintering aid, and sintering was performed at 1850°C for 2 h in an argon atmosphere without applied pressure. The major findings are summarized as follows:

1. All specimens exhibited low residual porosity (porosity < 2.61%), and the porosity decreased from 2.61 to 0.37% with an increase in additive content from 3 to 7 vol% owing to the increased mass diffusion at a high level of additive content. The high density achieved at a low temperature (1850°C) was attributed to (i) the low melting temperature of the Al-Y-Ca-Si-O-C liquid phase formed during sintering, (ii) the reduced evaporative loss of additives at the low sintering temperature, and (iii) the beneficial effect of an addition of 1 vol% α-SiC seed.
2. All the specimens exhibited a predominant β to α phase transformation. The dissolution of Al atoms in the SiC lattice during sintering...
created point defects (Al\textsubscript{53}, O\textsubscript{c}, V\textsubscript{Si}) and triggered the phase transformation. The retarded phase transformation with an increase in the additive content confirmed the diffusion-controlled kinetics of the phase transformation in the present case.

(3) All specimens exhibited elongated grains with a small volume fraction of equiaxed grains due to the predominant \(\beta\) to \(\alpha\) phase transformation (forming elongated platelet \(\alpha\)-SiC grains) and the growth of the initially added \(\alpha\)-SiC seeds during sintering. The gradual decrease in average grain size with an increase in additive content confirmed the diffusion-controlled kinetics of grain growth in the present case.

(4) The fracture toughness increased with an increase in additive content from 3 to 7 vol\%, and thereafter decreased gradually for 10 and 15 vol\% additive content. The high fracture toughness at 7 vol\% additive content was attributed to the well-interlocked, elongated SiC grains and optimal interfacial strength. The low fracture toughness at low additive content (3 vol\%) was attributed to an increase in transgranular fracture with poor crack–microstructure interaction. However, the poorly interlocked grains with a thick IGP provided easy cleavage along the grain boundaries, resulting in the poor crack–microstructure interaction and low fracture toughness at a high level of additive content. The hardness decreased gradually with an increase in additive content owing to an increased volume fraction of relatively soft IGP at a high level of additive content.

(5) The thermal conductivity decreased gradually with an increase in additive content due to the increased volume fraction of IGP with low thermal conductivity and increased phonon scattering with an increased volume of homophase- and heterophase-grain boundaries with small grain size at a high level of additive content.

(6) The typical values for flexural strength, fracture toughness, hardness, and thermal conductivity for the pressureless LPS-SiC ceramics with 7 vol\% of additives were 686 MPa, 5.4 MPa·m\(^{1/2}\), 26.3 GPa, and 70 W·m\(^{-1}\)·K\(^{-1}\), respectively.

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**Disclosure statement**

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**ORCID**

Rohit Malik https://orcid.org/0000-0001-8764-3321
Young-Wook Kim https://orcid.org/0000-0001-6275-0323

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