

Supporting Information

Robust Bulk Silicon Carbide Polymorphs Sintered from Collapsed Hollow Mesoporous Structure

Pengpeng Qiu^{1#}, Yi Zhou^{1#}, Yuqi Zhu¹, Barun Li¹, Beibei Gao¹, Weichao Bao^{2*},
Fangfang Xu², Yuchi Fan^{1*}, Lianjun Wang¹, Wan Jiang¹, Wei Luo^{1*}

¹State Key Laboratory of Advanced Fiber Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China.

²State Key Laboratory of High Performance Ceramics, Shanghai Institute of Ceramics, Shanghai 200050, China

Email: baoweichao@mail.sic.ac.cn; yuchifan@dhu.edu.cn; wluo@dhu.edu.cn

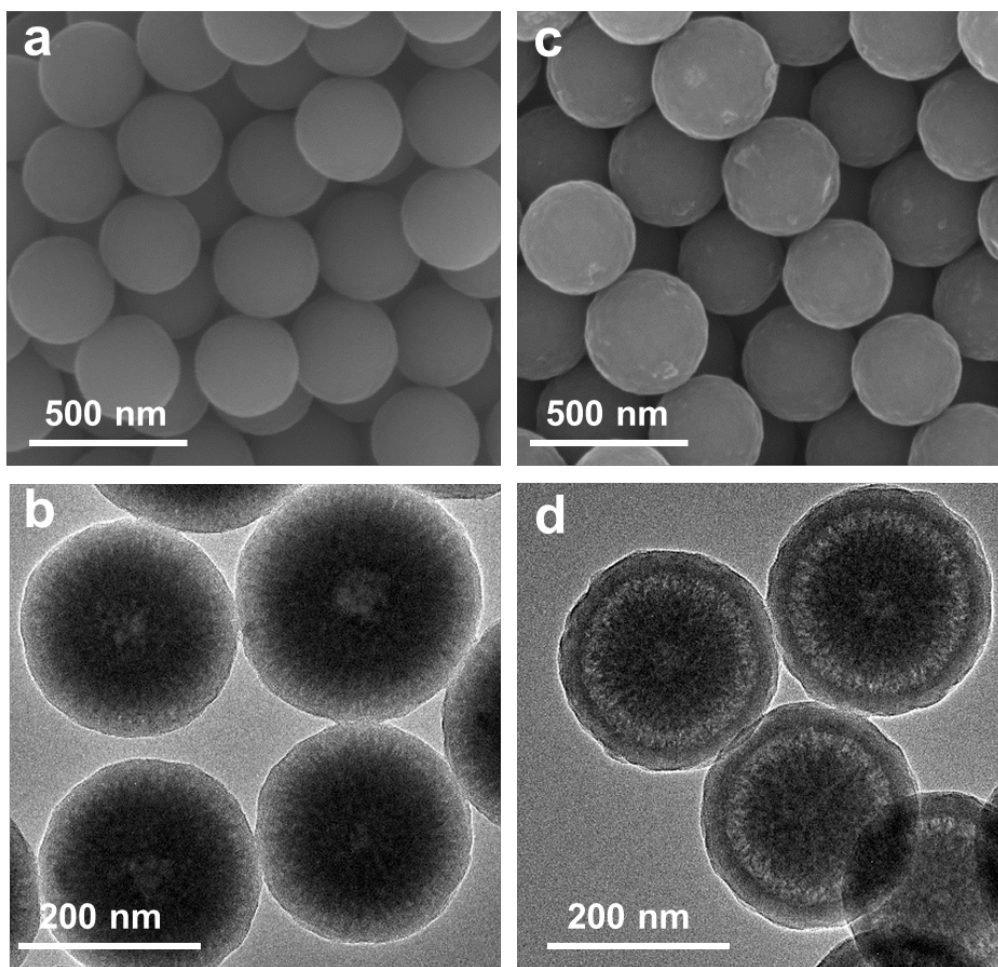


Fig. S1. SE SEM (a, c) and TEM (b, d) images of C@SiO₂-ns nanospheres, illustrating their well-defined spherical morphology with core-shell architecture. Panels (a) and (b) correspond to C@SiO₂-1s, while (c) and (d) show C@SiO₂-2s, both exhibiting uniform structural characteristics.

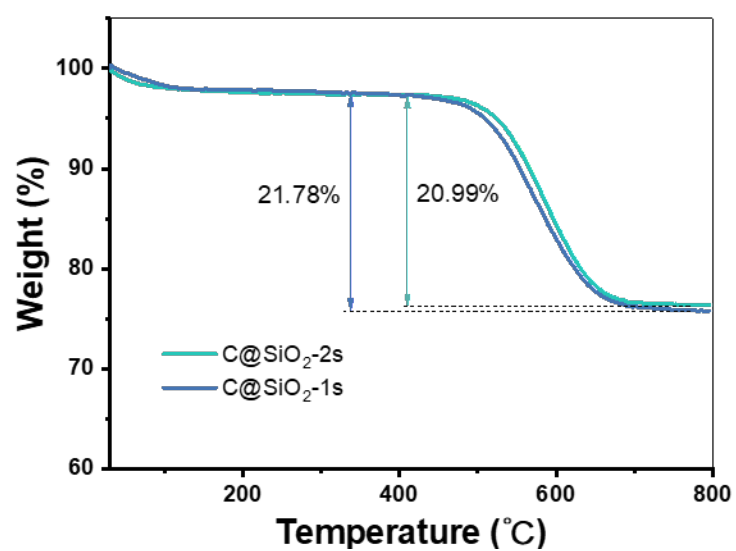


Fig. S2. Thermogravimetric analysis results for the core-shell C@SiO₂-ns composites, demonstrating consistent carbon content throughout the measurement.

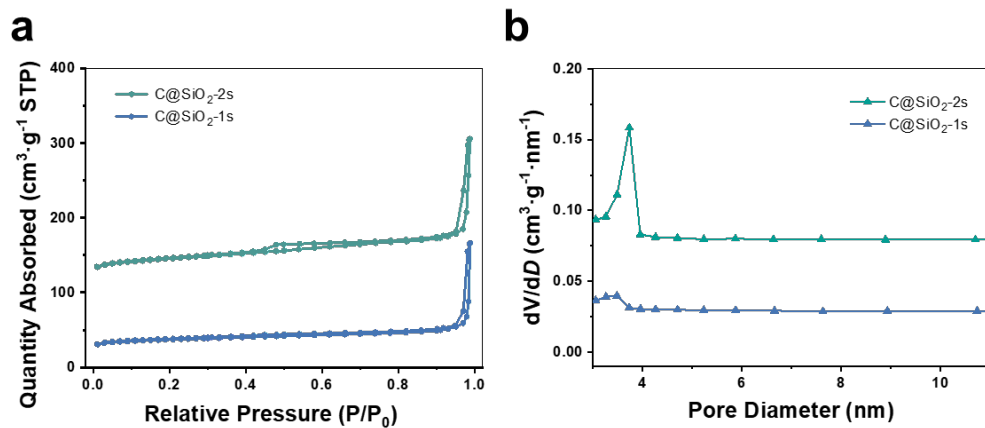


Fig S3. Nitrogen sorption isotherms and corresponding pore size distribution analysis of the C@SiO₂-ns nanospheres. These results clearly demonstrate the formation of an ordered mesoporous architecture, with the majority of mesopores exhibiting a uniform diameter centered around 3 nm.

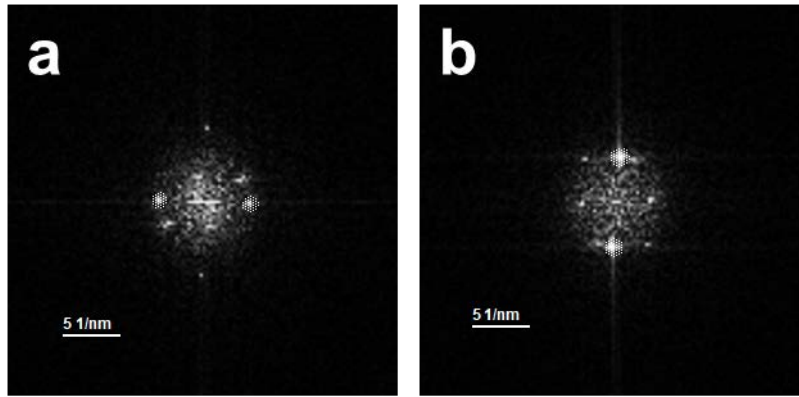


Fig. S4. (a, b) The FFT patterns corresponding to the selected regions (f_1) and (f_2) in Fig.1f, along with the masks employed for generating the iFFT images. The iFFT pattern was generated by applying symmetrical circular masks to selectively preserve the targeted diffraction spots along with their neighboring low-frequency components, while systematically removing all extraneous diffraction patterns and background noise.

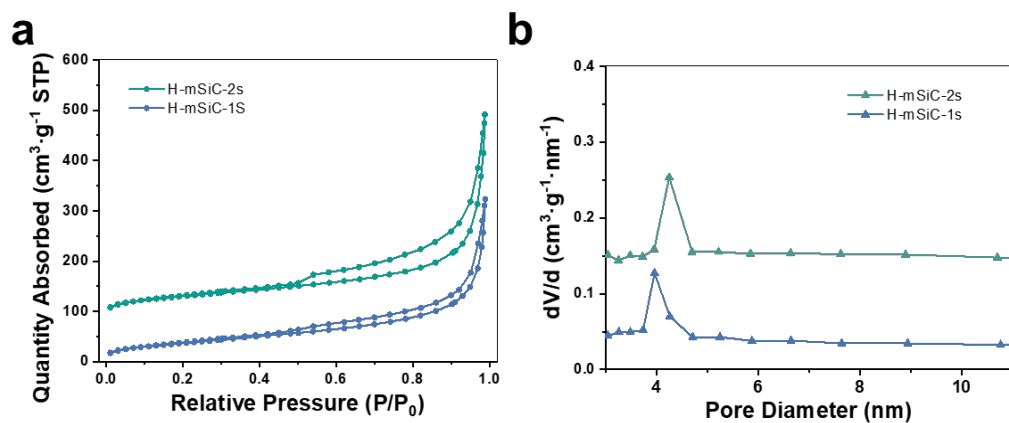


Fig S5. Nitrogen sorption isotherms and corresponding pore size distribution analysis of the H-mSiC-ns powders. These measurements clearly demonstrate the existence of an ordered mesoporous framework, with the majority of pores exhibiting a uniform diameter centered around 4 nm.

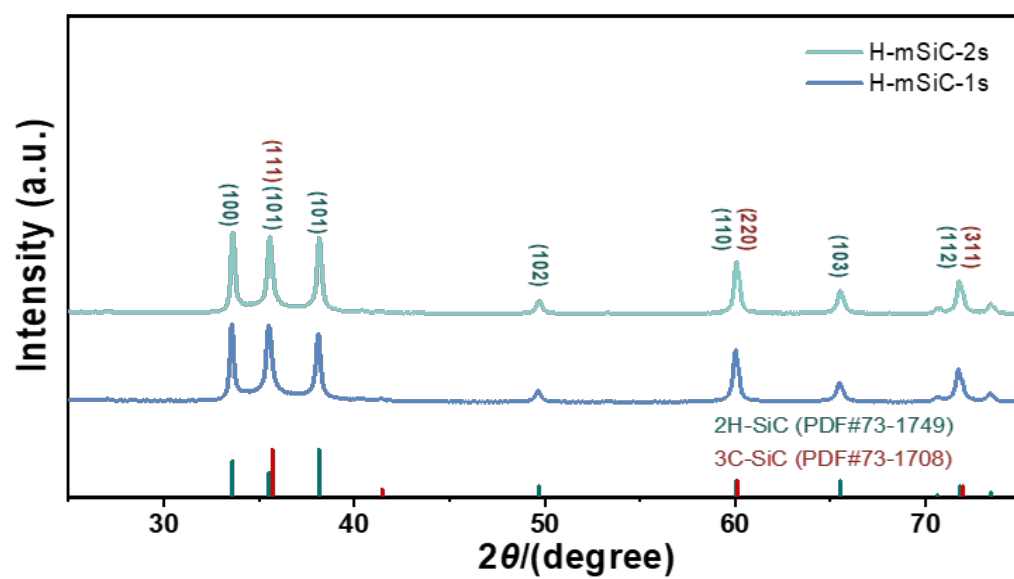


Fig. S6. XRD patterns of H-mSiC-1s and H-mSiC-2s powders, showing two distance phases of 2H and 3C.

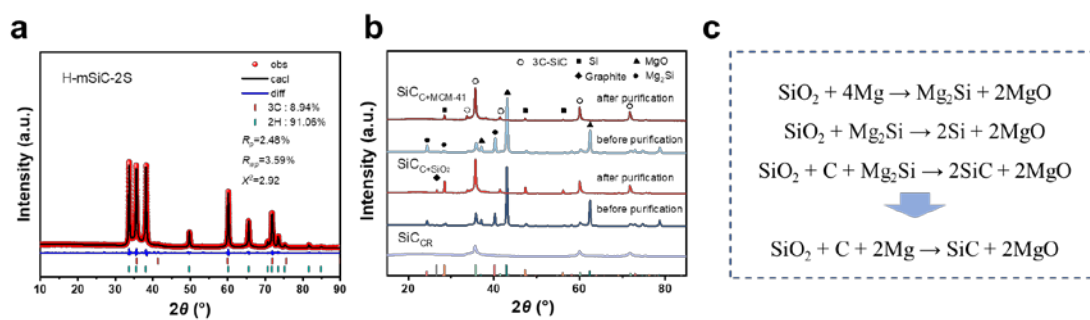


Fig S7. (a) Refined XRD patterns of H-mSiC-2s used for quantitative phase analysis, (b) Comparative XRD spectra of reference samples, and (c) The chemical equation representing the magnesiothermic reduction reaction.

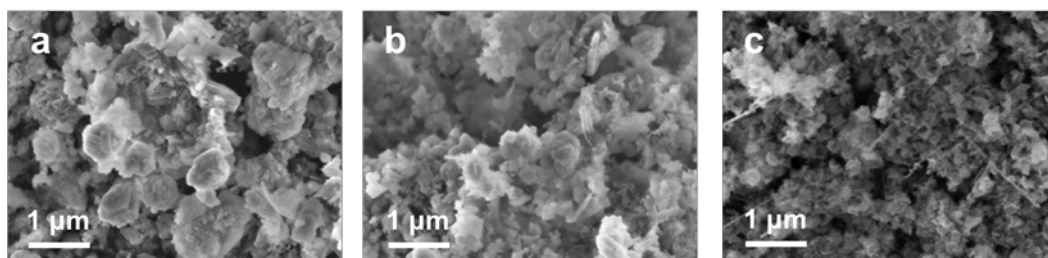


Fig S8. SE SEM images of (a) SiC_C+SiO₂, (b) SiC_C+MCM-41, and (c) SiC_{CR}, demonstrating consistently irregular surface morphologies with substantial contaminant presence in all specimens.

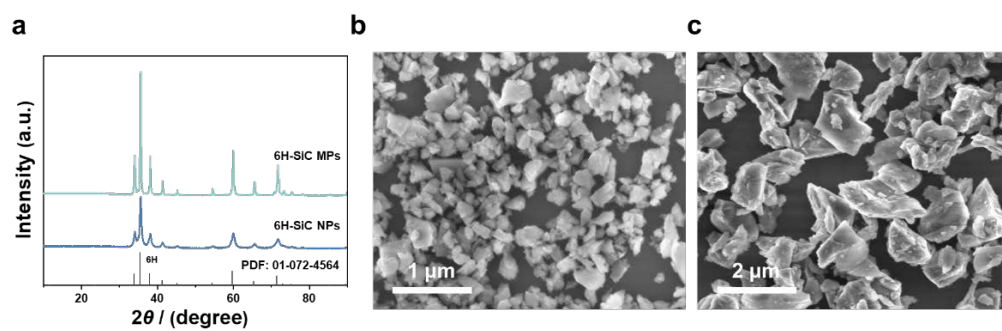


Fig. S9. The XRD patterns (a) and SE SEM images of 6H-SiC NPs (b) and 6H-SiC MPs (c).

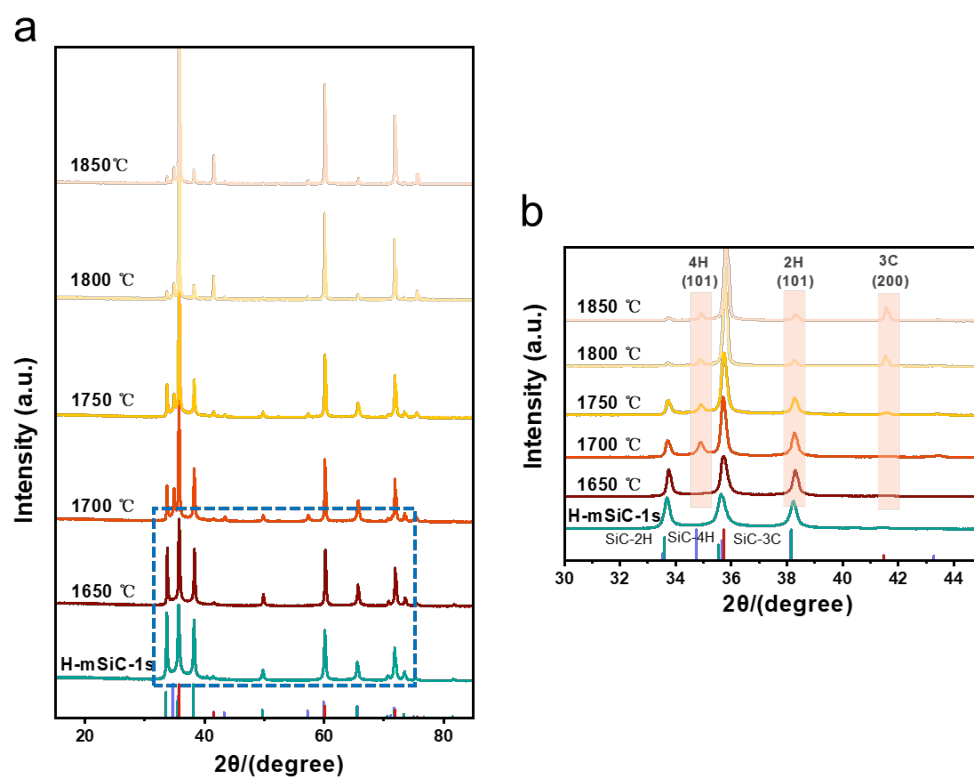


Fig. S10. The XRD patterns (a) coupled with detailed magnified views (b) of the H-mSiC-1s powders subjected to various sintering temperatures.

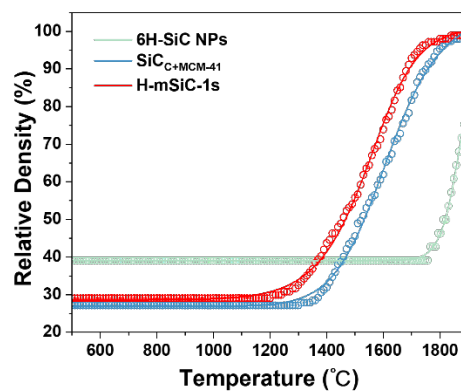


Fig. S11. The temperature-dependent variation in relative density curves during the condensation process, clearly demonstrating that porous powders initially exhibit lower density compared to nonporous 6H-SiC NPs, a phenomenon directly attributable to the intrinsic porosity present in the powder structure.

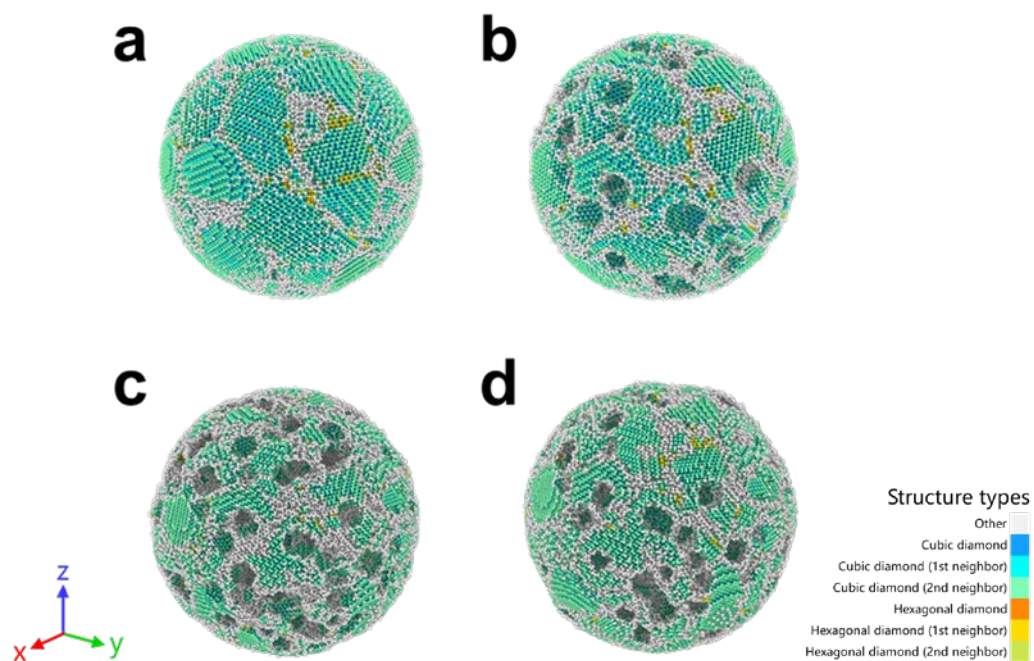


Fig. S12. 3D models for (a) 6H-SiC NPs, (b) $\text{SiC}_C+\text{MCM-41}$, (c) H-mSiC-1s, and (d) H-mSiC-2s.

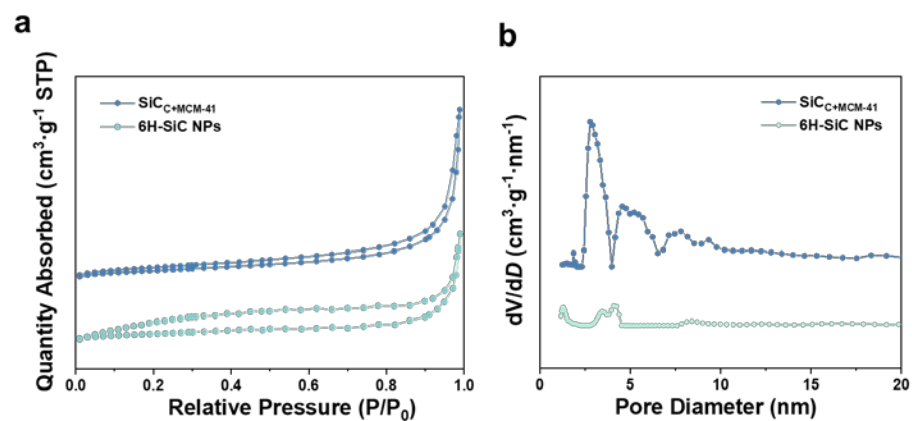


Fig. S13. (a) Nitrogen sorption isotherms and (b) corresponding pore size distribution of the commercial 6H-SiC NPs and $\text{SiC}_{\text{C+MCM-41}}$.

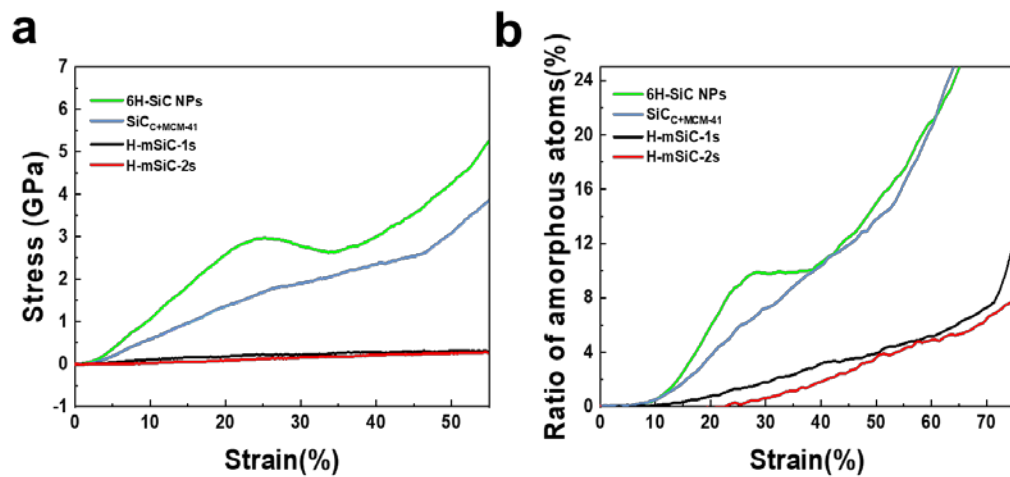


Fig. S14. The MSDs evolution of (a) Von Mises strain-stress and (b) strain-ratio relationships for amorphous atoms in various powder samples subjected to nanoindentation testing.

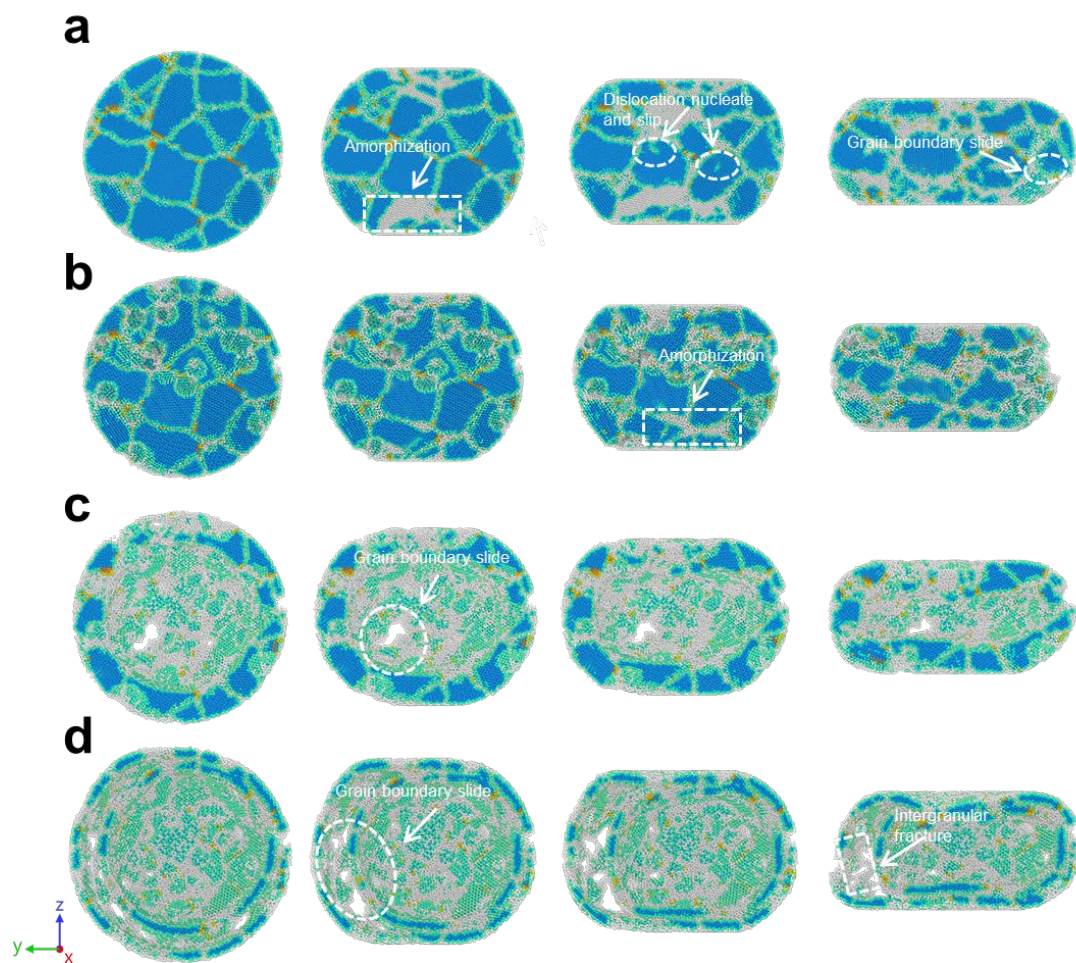


Fig. S15. The corresponding cross-sectional view of the three-dimensional models: (a) 6H-SiC NPs, (b) SiC_C+MCM-41, (c) H-mSiC-1s, and (d) H-mSiC-2s. The distinct boundaries between crystalline regions are clearly visible as parallel lines. In this representation, atomic positions are color-coded: blue denotes cubic phase atoms, while yellow indicates hexagonal phase atoms.

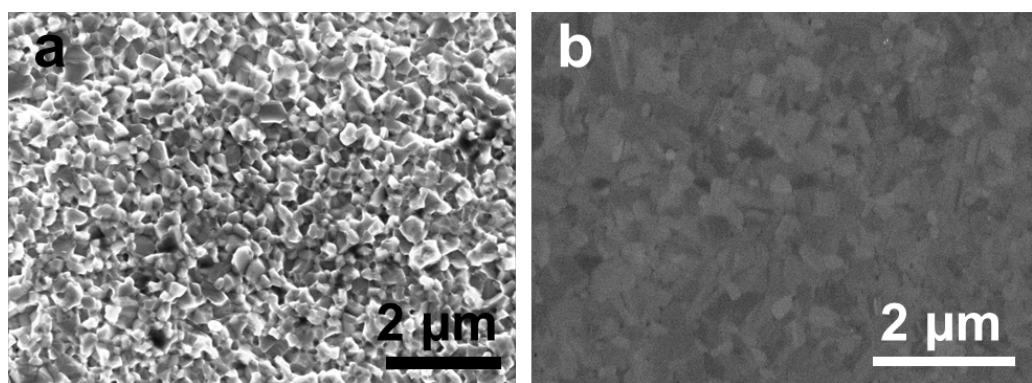


Fig. S16. Characterization of B-SiC-1750 ceramics: low-magnification BE SEM images of (a) fractured surface and (b) Ar ion polished surface.

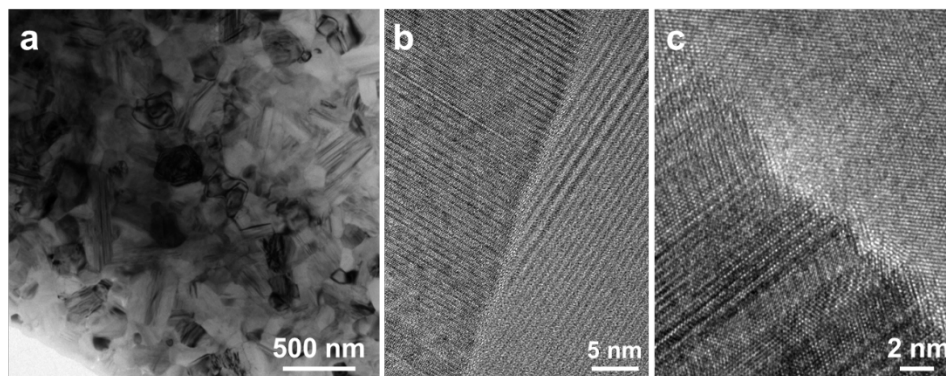


Fig. S17. (a) TEM and (b, c) HRTEM images of grain boundaries in B-SiC-1750 ceramics.

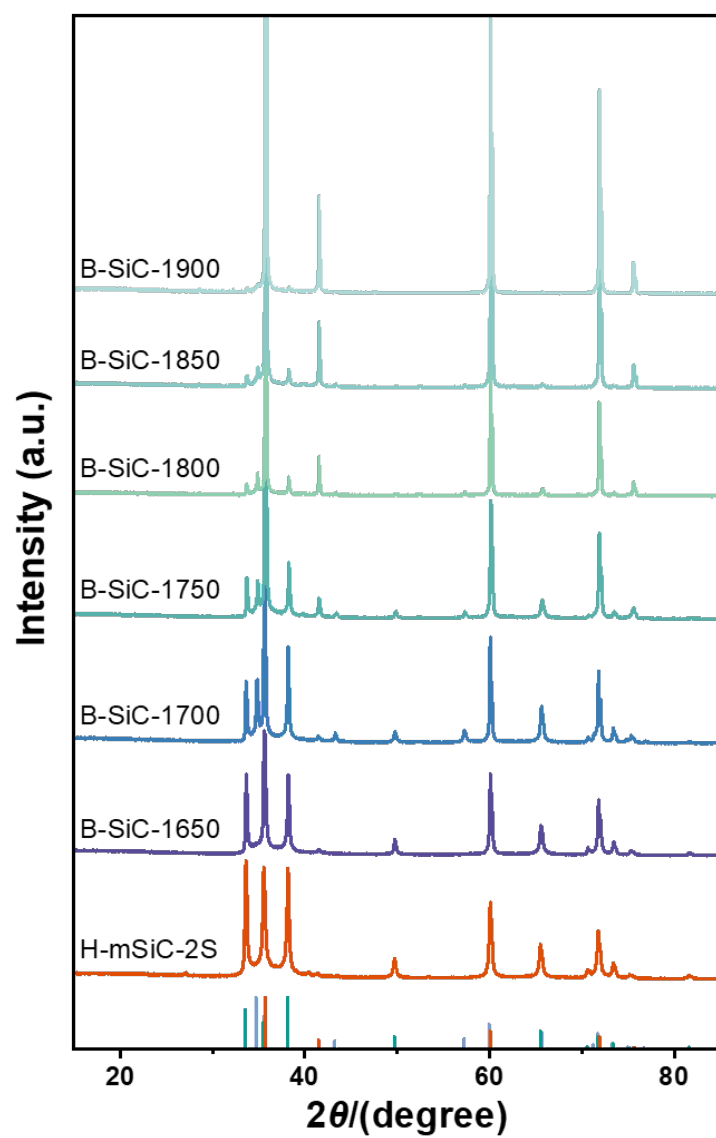


Fig. S18. XRD patterns of the B-SiC sintered at different temperatures.

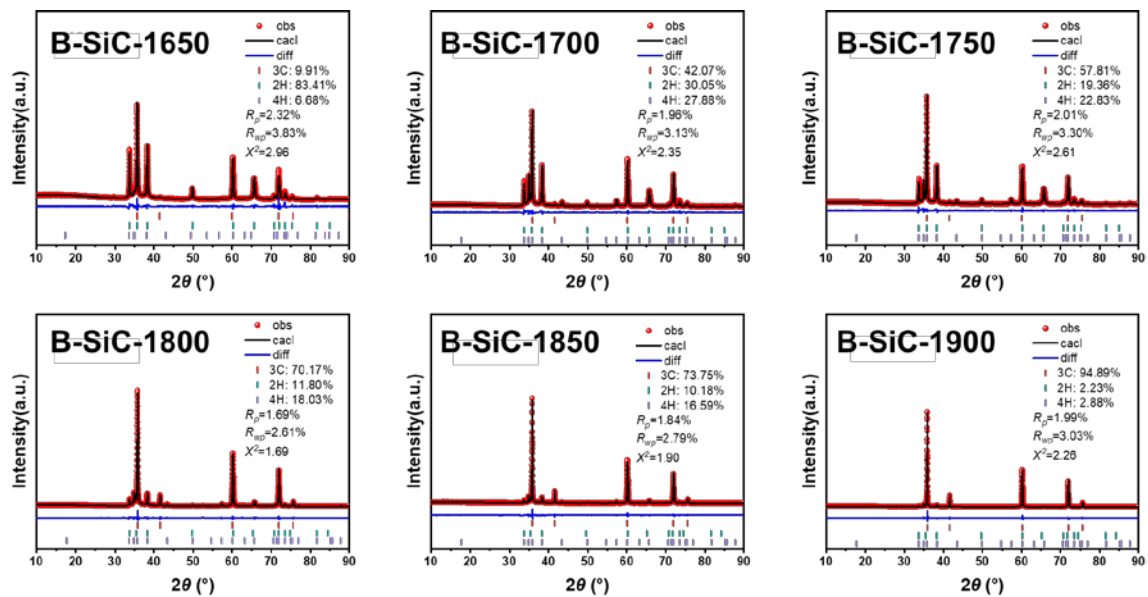


Fig. S19. The refined XRD patterns for different ceramics.

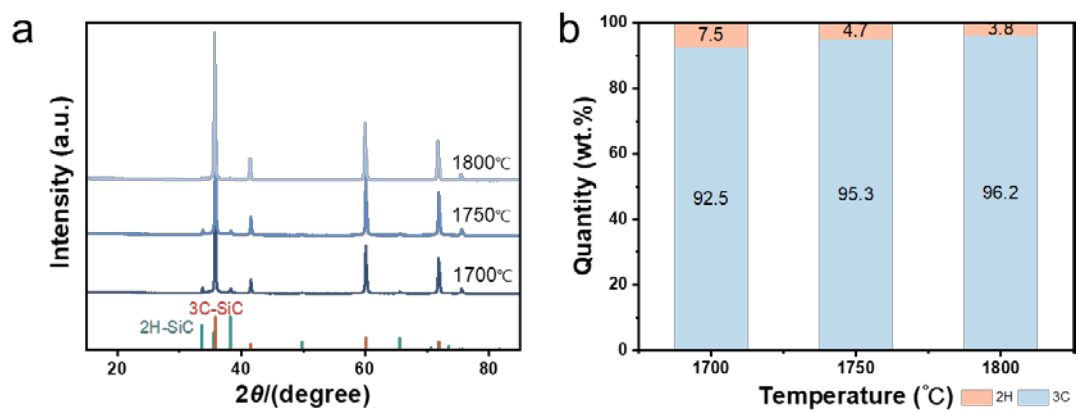


Fig. S20. (a) XRD patterns of B-SiC ceramics sintered at different temperature derived from H-mSiC-2s powder under pressureless sintering and (b) Quantitative phase determination

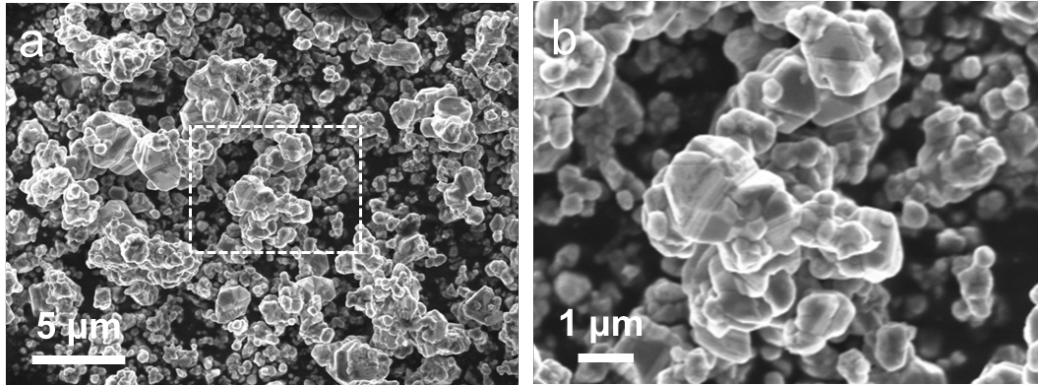


Fig. S21. (a) SE SEM image of the pressureless-sintered B-SiC ceramics fabricated from H-mSiC-2s powder, and (b) an enlarged view of the aggregated structure corresponding to the white rectangular region in (a).

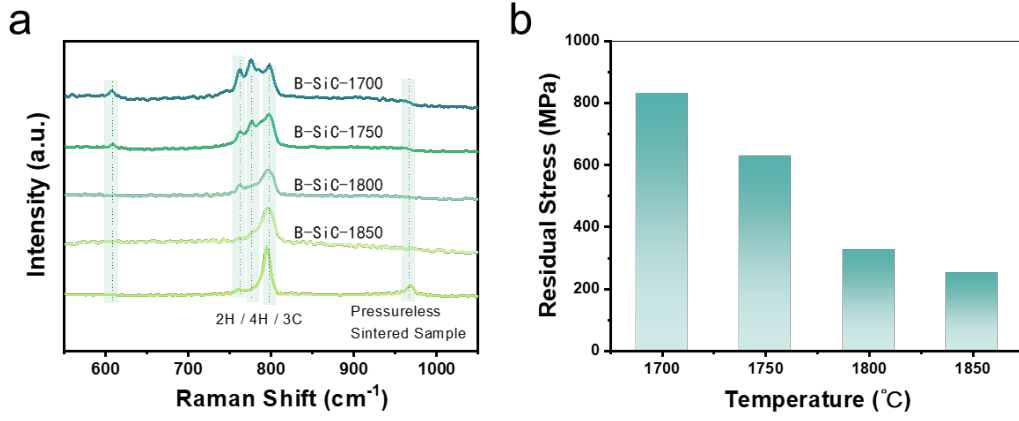


Fig. S22. (a) Raman spectra of B-SiC ceramics prepared at different temperature, and (b) corresponding residual stress calculated through equation $\sigma_{res} = k\Delta\omega$. Where σ_{res} is the residual stress, k is the piezospectroscopic constant, and $\Delta\omega$ represents the peak wavenumber shift between stress-free and stressed samples. In this study, a pressureless sintered sample at 1850 °C served as the stress-free reference.

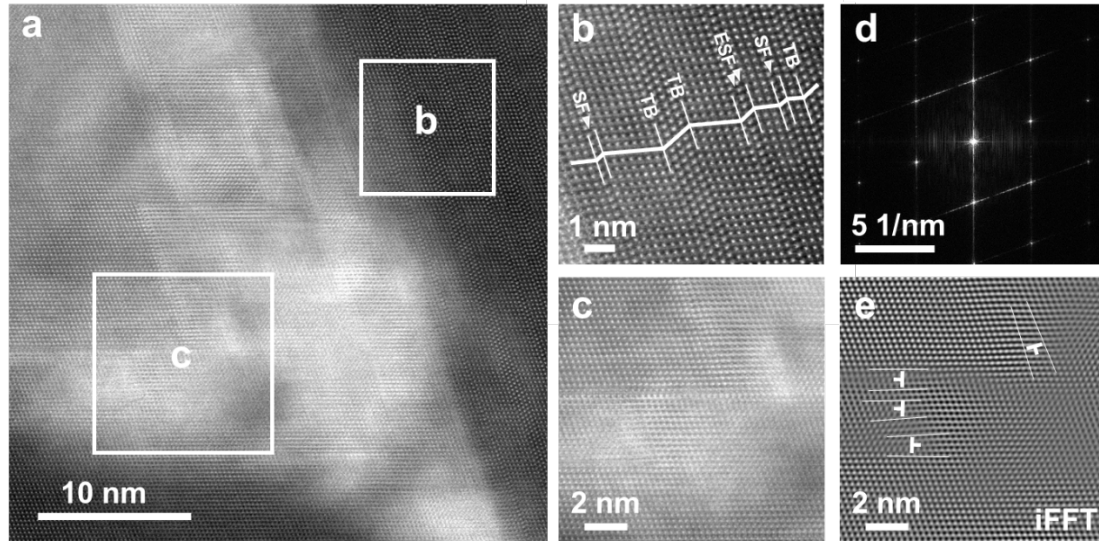
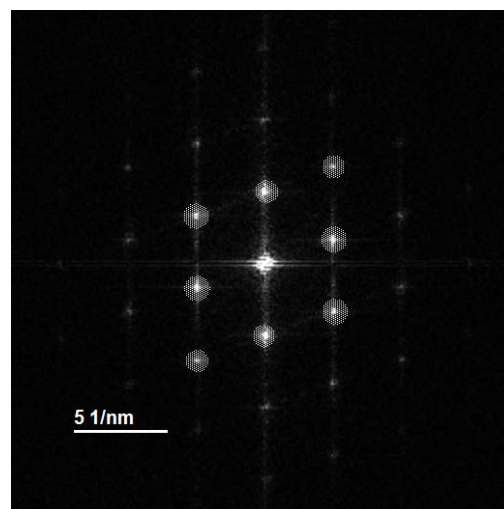


Fig. S23. Structural characterization of B-SiC-1750: (a) HAADF-STEM overview image with corresponding magnified views (b, c) revealing a high density of SFs, TBs, and L-C locks. The crystallographic analysis is further supported by (d) the FFT and iFFT patterns derived from region (b). The iFFT pattern (e) was generated by applying symmetrical circular masks to selectively preserve the targeted diffraction spots along with their neighboring low-frequency components, while systematically removing all extraneous diffraction patterns and background noise. The specific circular mask employed in the FFT pattern to produce this iFFT is presented below.



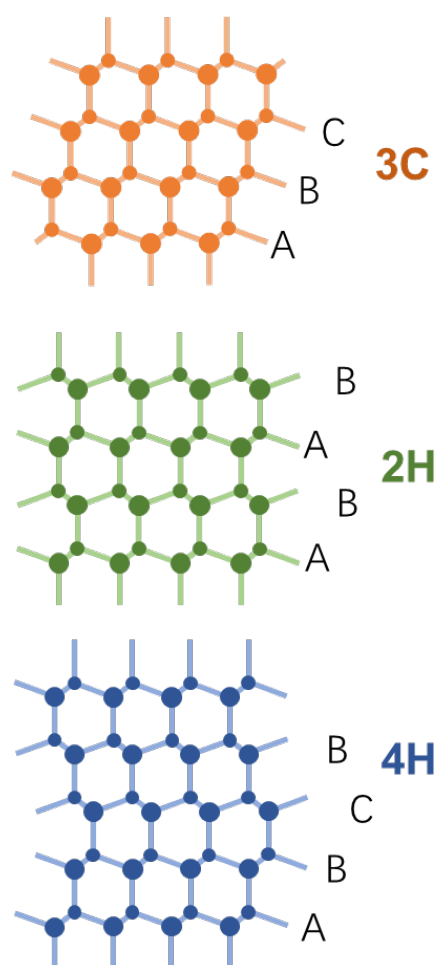


Fig. S24. Schematic illustration for 3C, 2H and 4H-SiC phases.

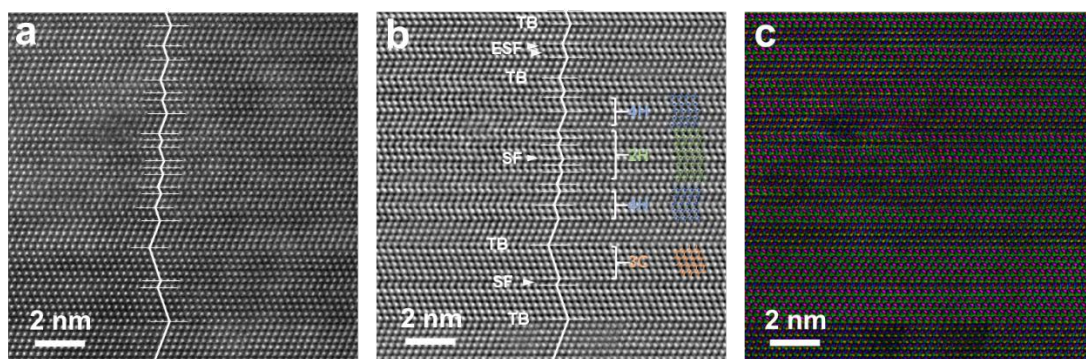


Fig. S25. (a and b) HAADF-STEM images and (c) iDPC of B-SiC-1750, clearly showing SiC coherently embedded 2H and 4H polytypes.

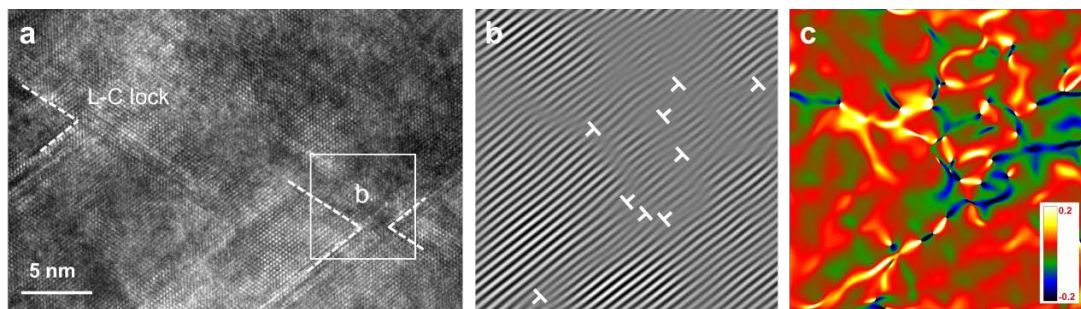
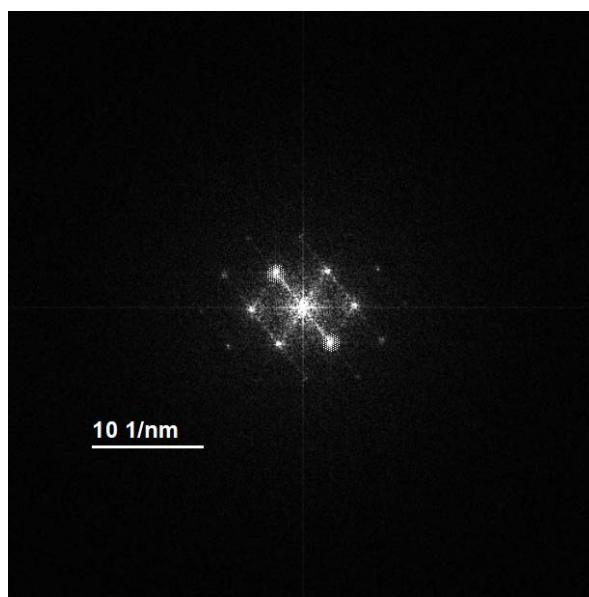


Fig. S26. (a) HAADF-STEM image, (b) corresponding IFFT pattern showing the L-C locks, and (c) GPA mapping. The iFFT pattern (b) was generated by applying symmetrical circular masks to selectively preserve the targeted diffraction spots along with their neighboring low-frequency components, while systematically removing all extraneous diffraction patterns and background noise. The specific circular mask employed in the FFT pattern to produce this iFFT is presented below.



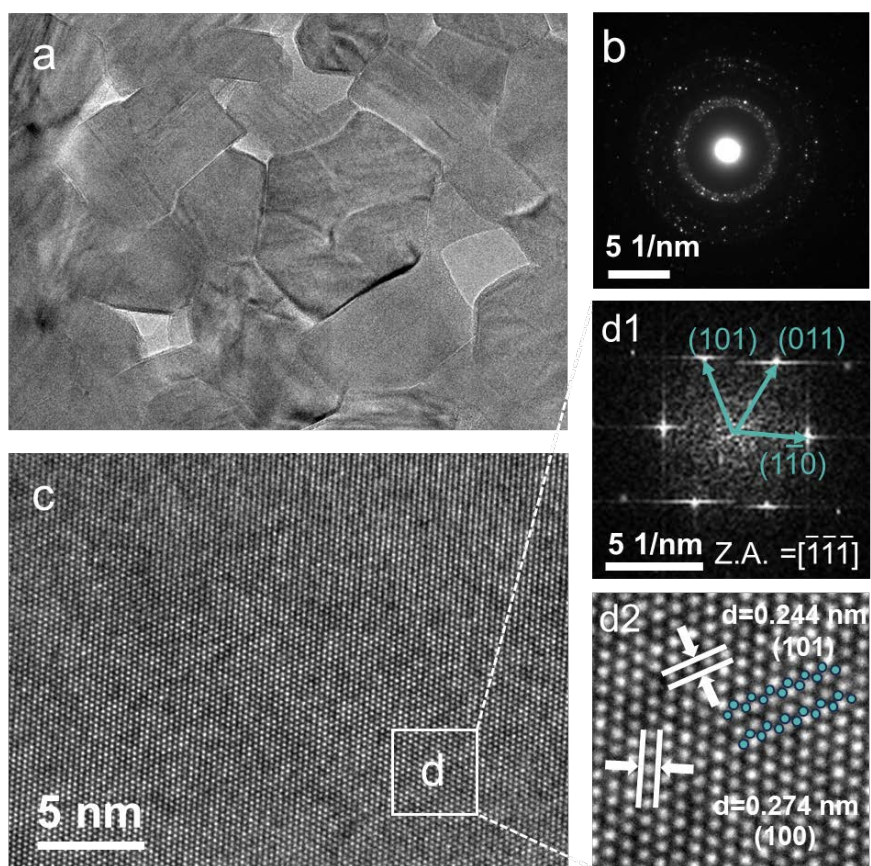


Fig. S27. Microstructure characterization of B-SiC-1650 ceramics: (a) low-magnification TEM image and (b) corresponding SAED pattern. (c) HAADF image and (d) corresponding FFT pattern (d₁) and enlarged HAADF image from d (d₂).

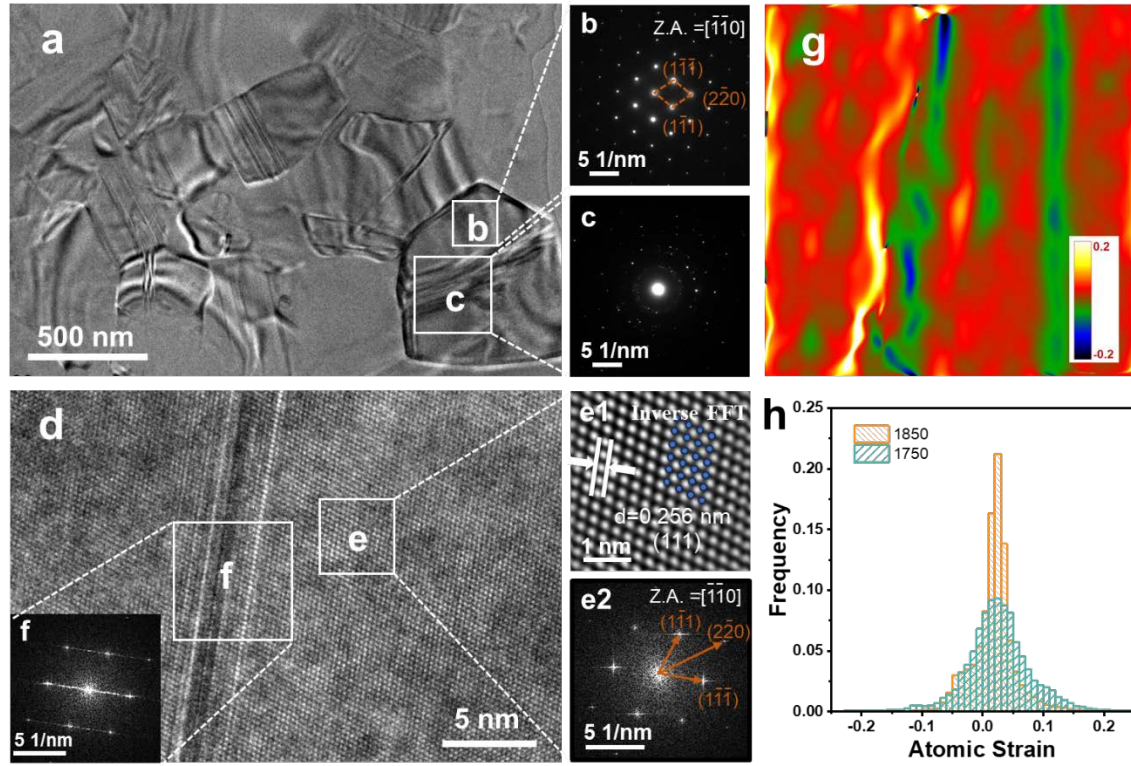
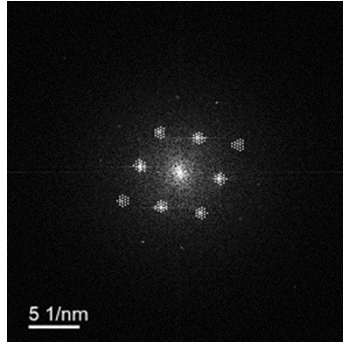


Fig. S28. Microstructure characterization of B-SiC-1850 ceramics: (a) low-magnification TEM image and (b, c) its corresponding SAED pattern in selected area. (d) HAADF image and its corresponding FFT pattern (f, e₂) and iFFT pattern (e₁). (g) GPA mapping and (h) corresponding atomic strain distribution. The iFFT pattern (e₁) was generated by applying symmetrical circular masks to selectively preserve the targeted diffraction spots along with their neighboring low-frequency components, while systematically removing all extraneous diffraction patterns and background noise. The specific circular mask employed in the FFT pattern to produce this iFFT is presented below.



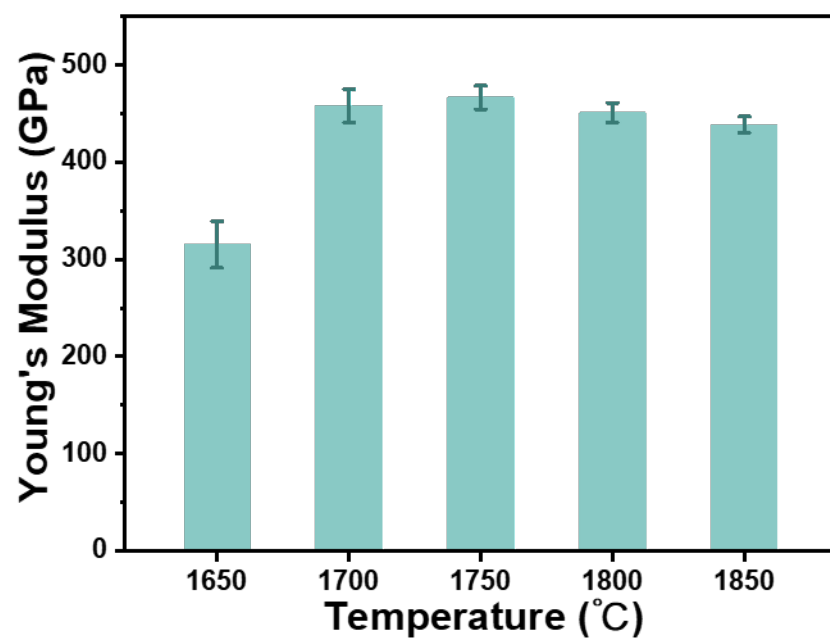


Fig. S29. Nanoindentation Young's modulus of bulk SiC ceramics derived from H-mSiC-2s powders sintered at temperatures ranging from 1650 to 1850 °C.

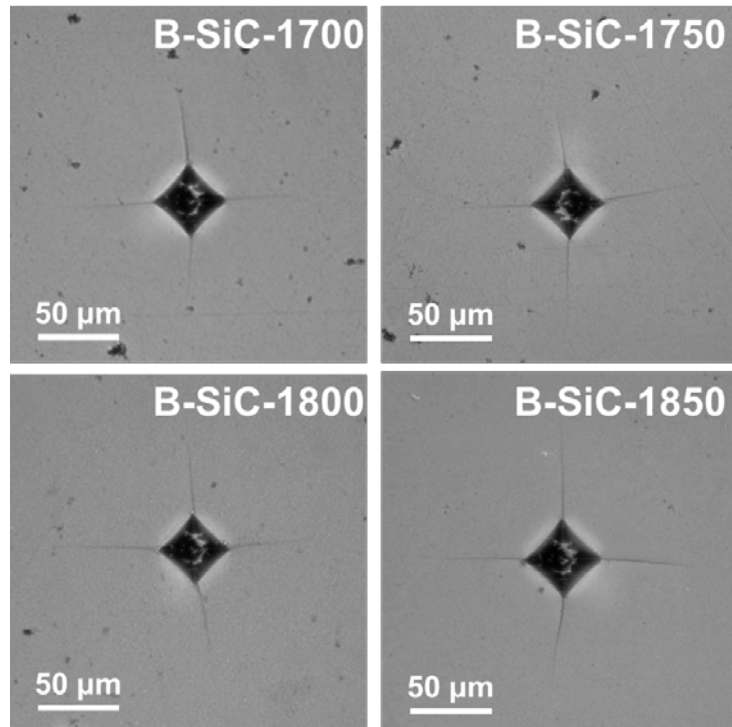


Fig. S30. Visual examination of Vickers hardness measurements across various ceramic materials.

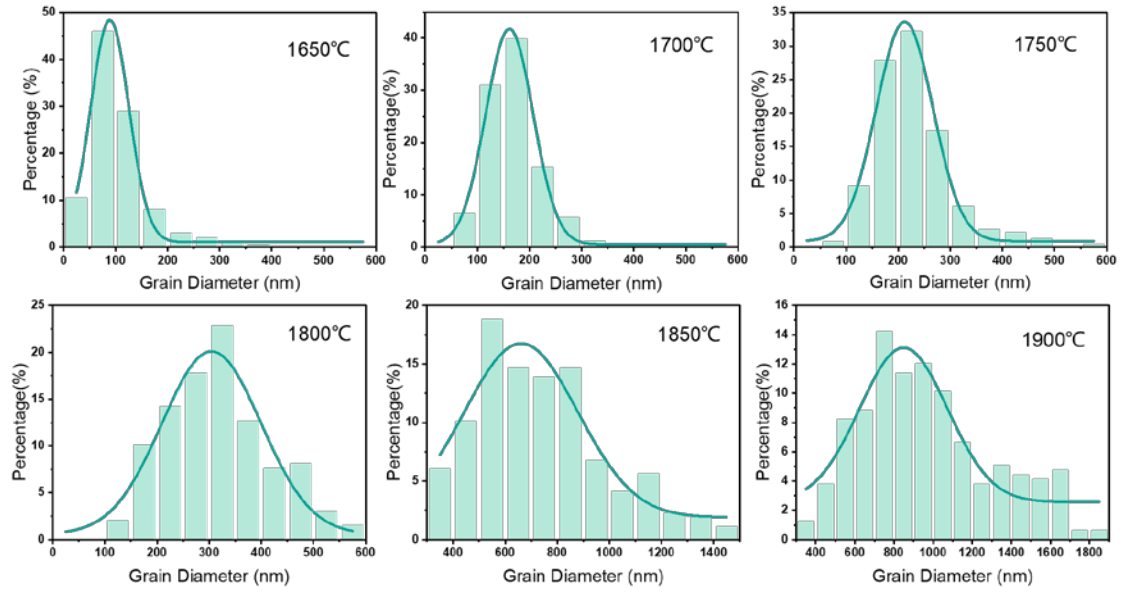


Fig. S31. Grain size distribution of B-SiC ceramics synthesized through SPS of H-mSiC-2S at different temperature.

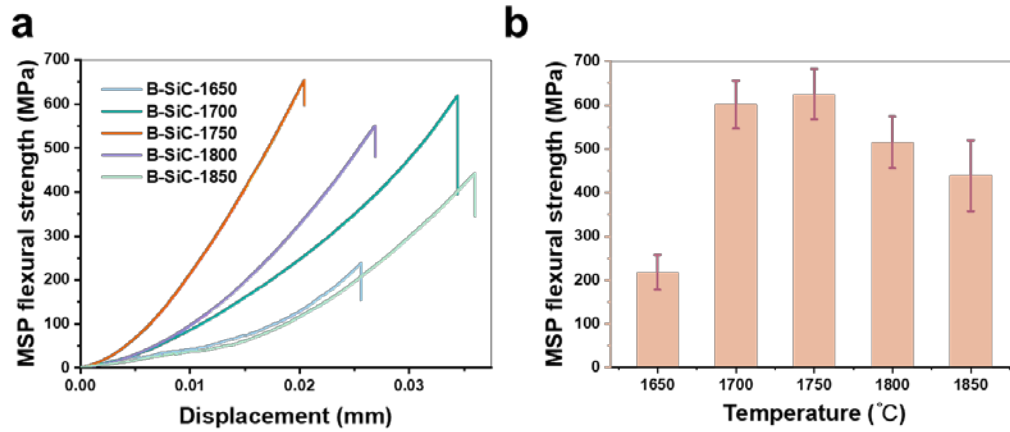


Fig. S32. (a) Representative flexural stress–displacement curves obtained from MSP testing for 10 mm diameter bulk SiC ceramics sintered at various temperatures, and (b) the resulting MSP flexural strength values.

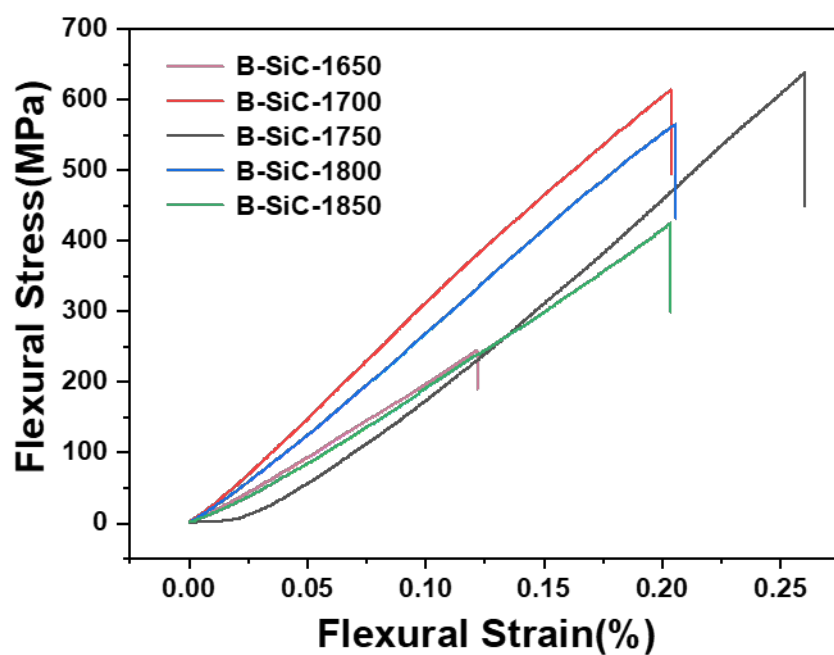


Fig. S33. Representative flexural stress–displacement curves obtained from TPB testing for 30 mm diameter bulk SiC ceramics sintered at various temperatures

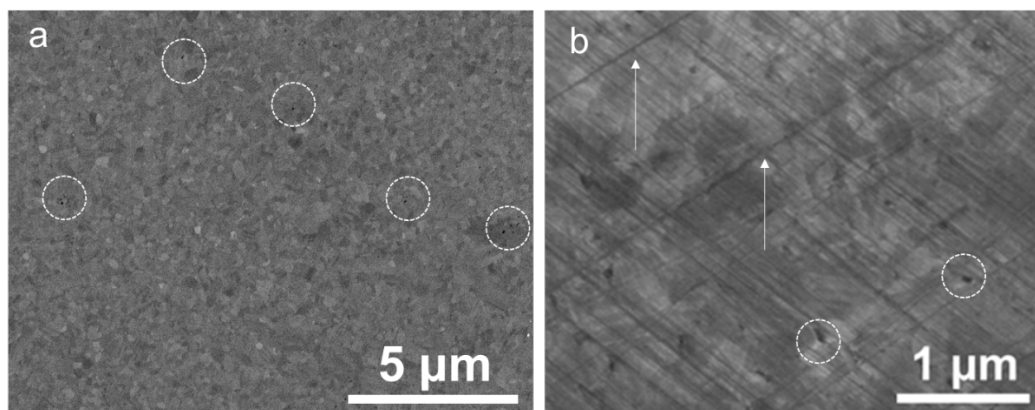


Fig. S34. Low-magnification SE SEM micrographs of (a) Ar ion polished surface (b) mechanical polished surface.

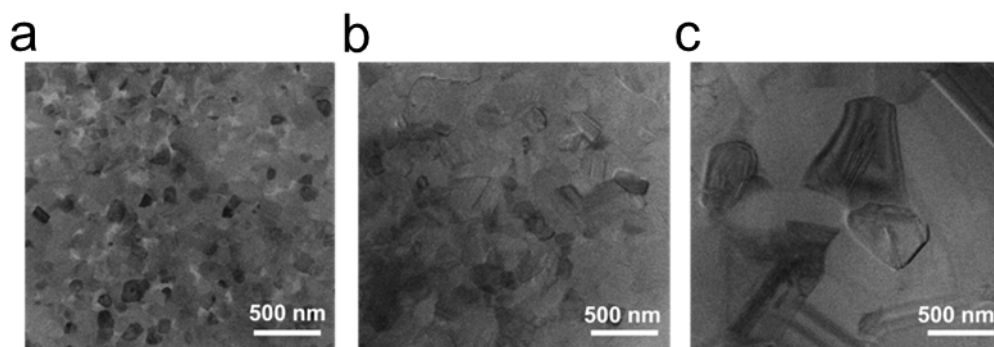


Fig. S35. TEM images of B-SiC-1650 (a), B-SiC-1750 (b), and B-SiC-1850 (c) ceramics, showing the growth of grain size with the increase of temperature.

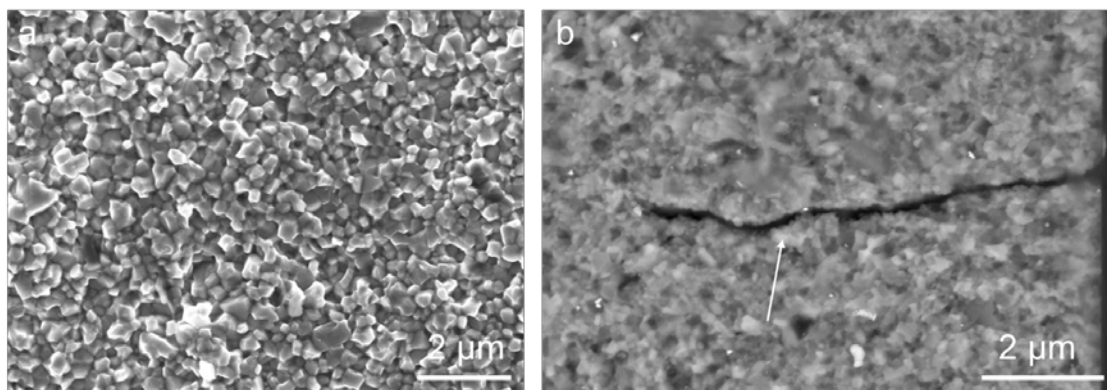


Fig. S36. Low-magnification BE SEM images of fractured surface of B-SiC-1750 ceramics: (a) showing the intergranular fracture and (b) showing the crack deflection.

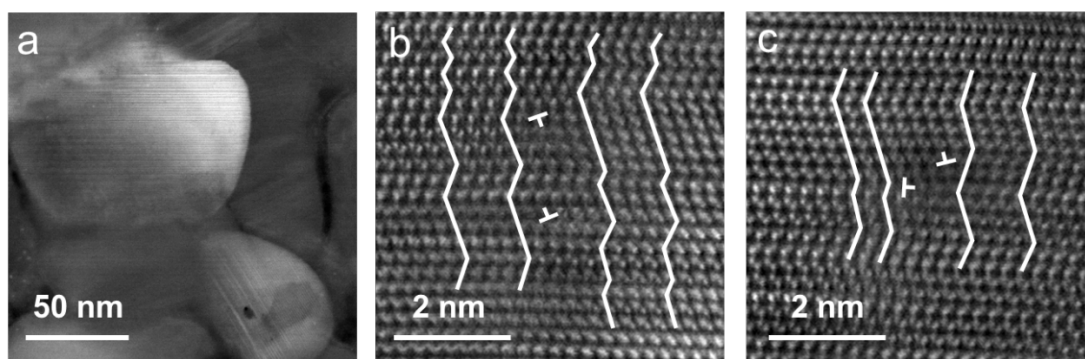


Fig. S37. (a) STEM image of the indentation impression region, and (b-c) corresponding HAADF-STEM images, showing structural transitions between SFs and twins.

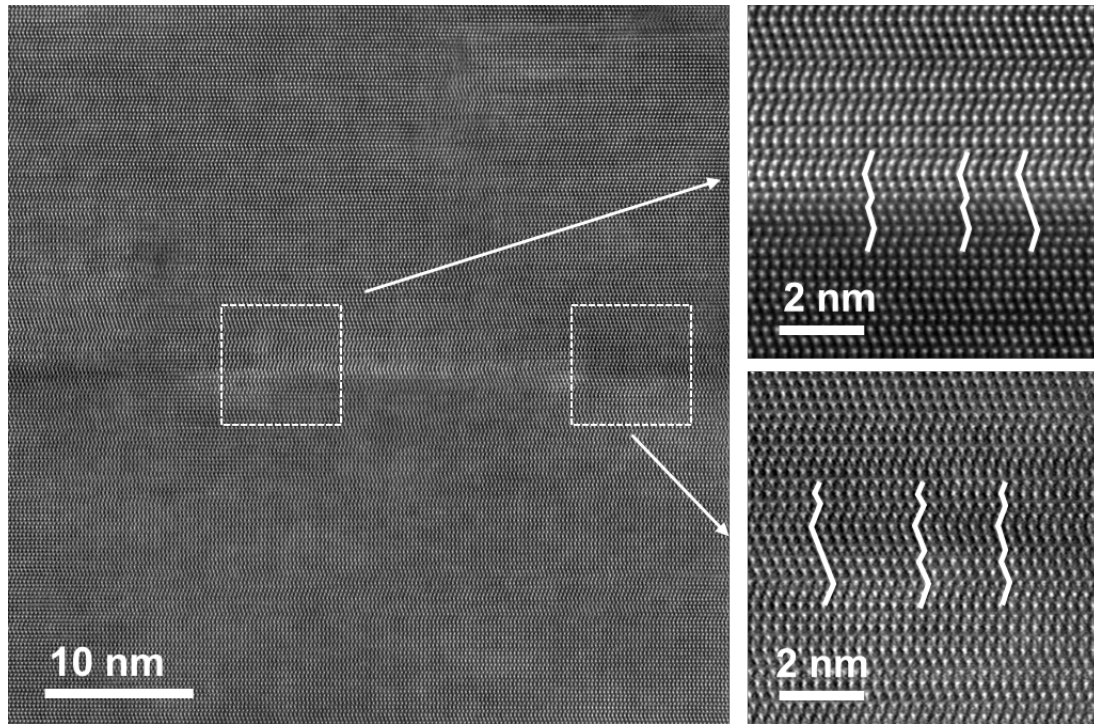


Fig. S38. HADF images of the indentation impression region, showing that the generation of stress-induced dislocations leads to the coexistence and transformation of SFs and twinning within the same atomic layer.

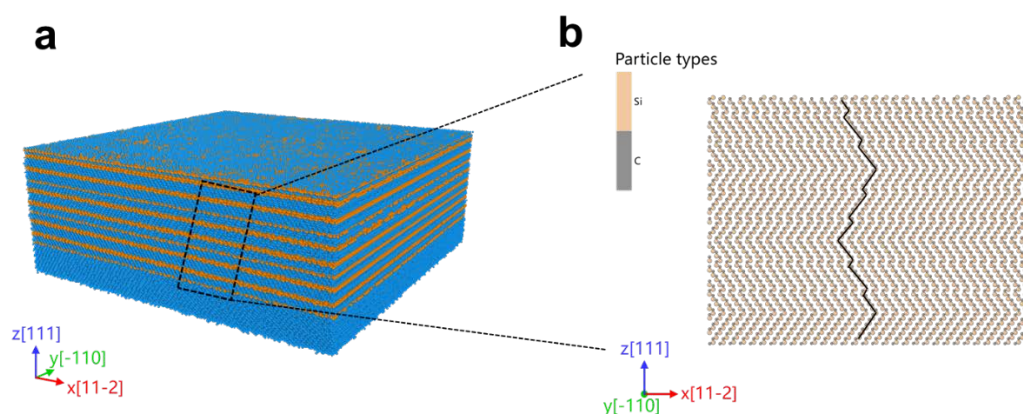


Fig. S39. (a) An example of 3C-SiC structure with SFs and TBs. Atoms are colored according to a structure identification algorithm for diamond lattice. Pristine diamond lattice is represented by blue atoms, whilst SFs and TBs are shown in orange, (b) Schematic illustration of the atomic arrangement of SFs and TBs in 3C-SiC

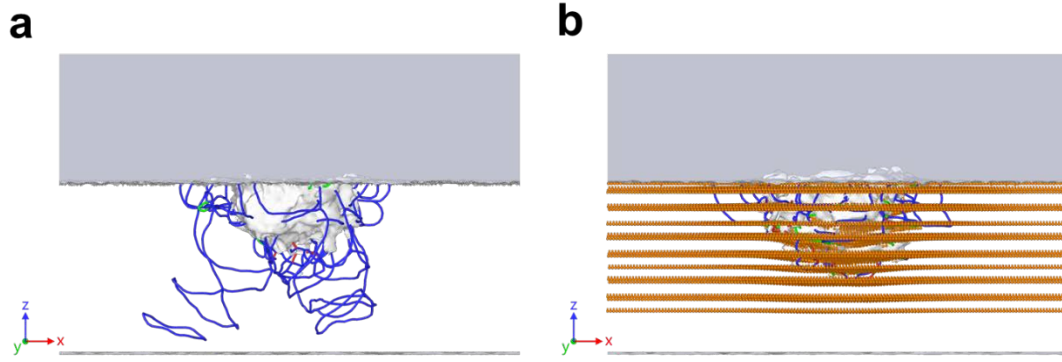


Fig. S40. Dislocation microstructures in (a) SC-SiC and (b)SF/TB-SiC under nanoindentation after full loading. Defects and dislocations are abstracted and colored with the DXA method.

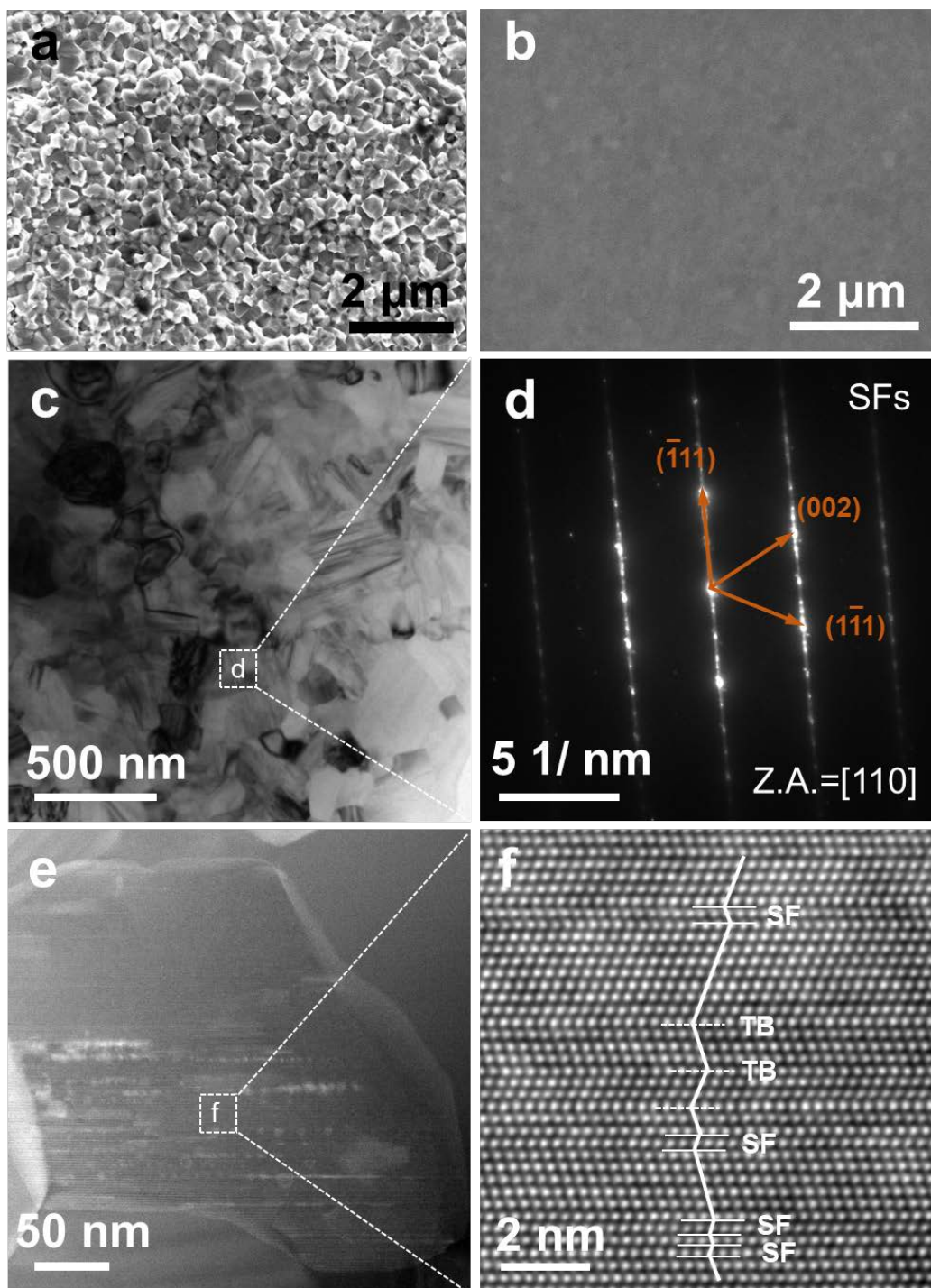


Fig.S41. Characterization of B-SiC-1750 ceramics in 30 mm diameter: SEM images of (a) fractured surface and (b) polished surface. (c) TEM image and (d) FFT pattern of corresponding regions, (e) HAADF image and (f) corresponding atomic structure showing the similar SFs and TBs.

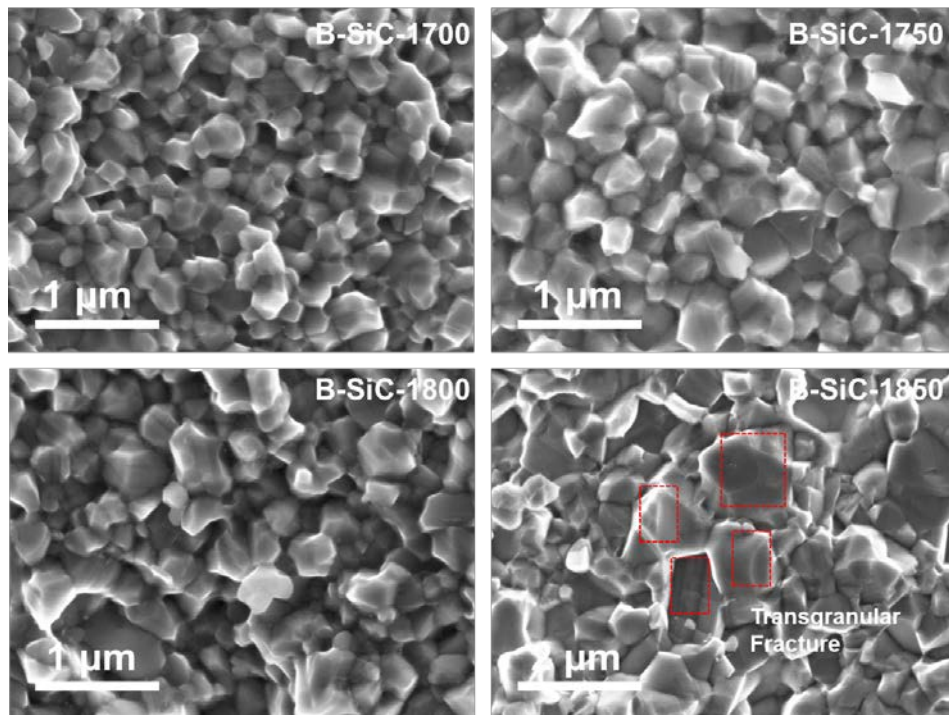


Fig. S42. SEM images of fracture surfaces of bulk SiC ceramics sintered at 1700–1850 °C after TPB tests.

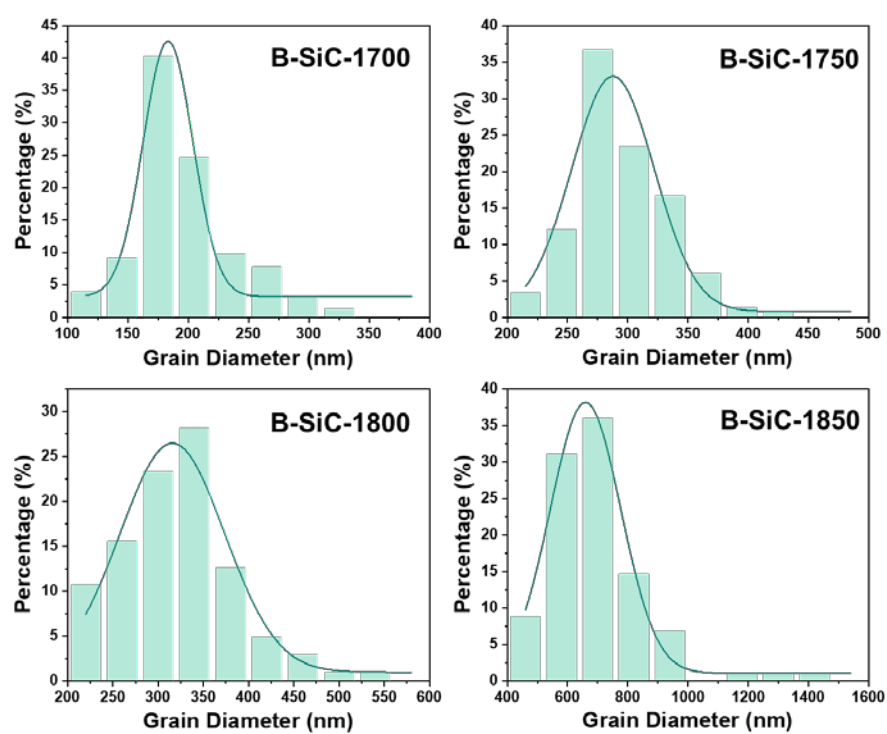


Fig. S43. Grain size distribution of bulk SiC ceramics sintered at 1700–1850 °C obtained from fracture surface analysis after TPB test.

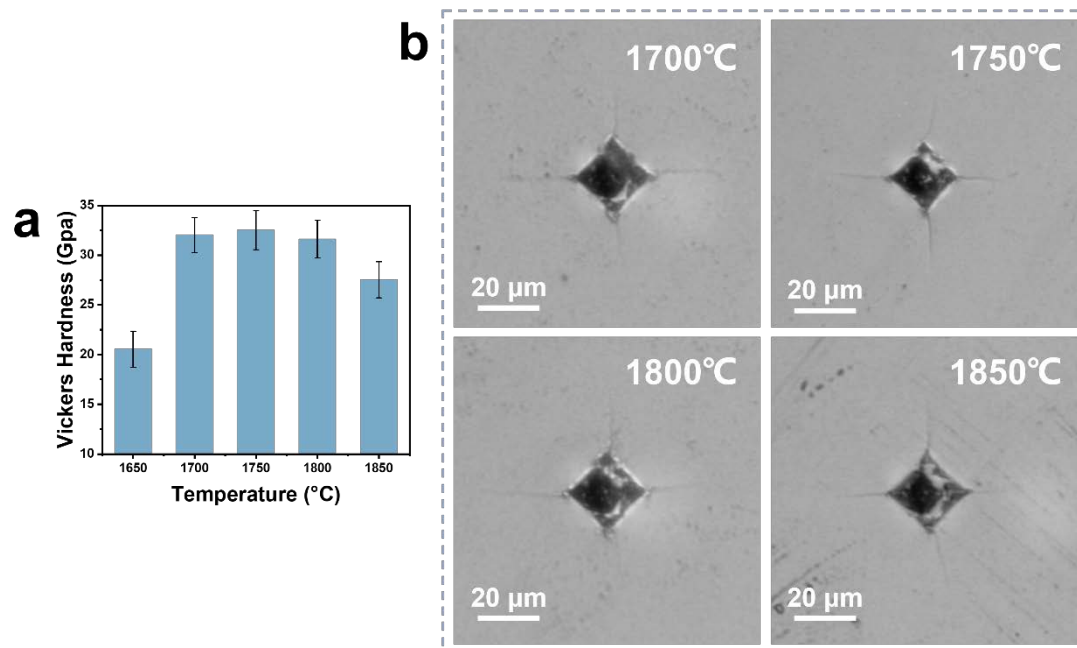


Fig. S44. Vickers hardness measured under a 1 kgf load (a) and corresponding indentation images of SiC ceramics sintered at different temperatures (b).

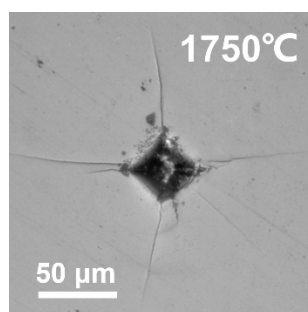


Fig. S45. Vickers indentation of SiC ceramic measured under a 5 kgf load.

Table S1 The physicochemical properties of the different samples.

Sample	BET surface area (m²/g)	Average pore size (nm)	Pore volume (cm³/g)
C@SiO ₂ -1s	159.1	3.5	0.26
C@SiO ₂ -2s	169.1	3.7	0.32
H-mSiC-1s	142.9	4.0	0.50
H-mSiC-2s	171.0	4.3	0.63

Table S2 Comparison of the flexural strength across specimens of varying dimensions.

T (°C) \ Specimen size	Flexural strength (MPa)			
	10 mm (MSP)	20 mm (TPB)	30 mm (TPB)	RSD (%)
1650	217.8 ± 40.11	262.91 ± 49.86	231.46 ± 18.95	9.74441
1700	601.13 ± 54.6	575.91 ± 35.84	595.81 ± 18.77	2.24957
1750	624.91 ± 57.3	621.39 ± 29.94	625.32 ± 22.3	0.34628
1800	514.76 ± 59.07	522.6 ± 35.97	539.15 ± 23.27	2.36944
1850	438.42 ± 81.5	406.81 ± 29.01	409.95 ± 15.56	4.16224

Note: To quantify the influence of specimen size on the measured strength, the relative standard deviation (RSD) was calculated using the strength values obtained from specimens with three different diameters at the same sintering temperature. The RSD was defined as:

$$\text{RSD} = \frac{s}{\bar{\sigma}} \times 100\%$$

where $\bar{\sigma}$ is the arithmetic mean of the strength values and s is the corresponding standard deviation ($n = 3$). This metric provides a normalized measure of the strength dispersion induced by specimen size.

Table S3 Comparative table of the sintering and mechanical performance.

	Sintering method	Absolute density	Relative density (%)	Grain size	Flexural strength (MPa)	Test method and dimensions	Vickers hardness (GPa)	Load (N)	Ref.
1	HP (2050°C , 40 MPa)	3.19	99.5	1 μm	453.7±44.9	TPB (2 *1.5*25 mm)	24.9 ± 0.8	20	[1]
2	SPS (1750°C , 80 Mpa)	3.15	98	1.1 μm	461 ± 15	TPB (3*4*20mm, span 16mm)	26.3±0.6	9.8	[2]
3	SPS (1860°C , 60 Mpa)	3.16	98.5	-	395	TPB (3*4*35mm, span 25mm)	28.5	20	[3]
4	SPS (1800°C , 30 MPa)	3.17	98.6	800 nm	592 ± 31	TPB (2*1.5*23mm, span 20mm)	28.3 ± 0.3	49	[4]
5	PLS (2000°C)	3.05	95	-	298.3±39.5	TPB(3*4*25mm, span 20 mm)	26.0±0.8	10	[5]
6	PLS (2130°C)	-	-	1.2 μm	425	TPB (2 *1.5*25 span 20mm)	27.28	4.9	[6]
7	SPS (1750°C , 50 MPa)	3.12	97.3	-	380	TPB (2*3*18mm, span 14mm)	26.68	9.8	[7]
8	HTPVT (2300°C)	3.19	99.3	100um	360	TPB (span 16mm)	29	9.8	[8]
9	HTPVT (2350°C)	3.21	99.9	-	290 ± 34	TPB (2 *1.5*25 span 20mm)	29.7 ± 0.6	9.8	[9]
10	SPS (2050°C , 69MPa)	3.18	99.1	-	490	TPB (3*4*20mm)	32	20	[10]
11	PLS (2000°C)	3.14	97.94	-	394 ± 18	TPB (2 *1.5*25 mm span 20mm)	27.2 ± 1.3	4.9	[11]
12	HP(2100°C , 40MPa)	3.19	99.5	-	533	TPB (3*4*36mm, span 30mm)	24.34	49	[12]
13	PLS(2000°C)	3.16	98.53	-	350	TPB (3*4*25mm,	27.1 ± 0.7	10	[13]

						span 20mm)			
14	PLS(2150°C)	3.06	95.3	-	296	TPB (3*4*35mm)	25.5	9.8	[14]

Reference

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