

Supporting Information

Temperature-invariant superelastic, fatigue resistant, and binary-network structured silica nanofibrous aerogels for thermal superinsulation

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Supplementary Methods

Fabrication of flexible SiO₂ nanofibers

The SiO₂ nanofibers were prepared by the combination of sol-gel method and electrospinning reported in our previous work.^[1-2] First, SiO₂ precursor sol solution was prepared by mixing TEOS, H₂O, EtOH, C₂H₂O₄ with a molar ratio of 1:3.57:0.71:0.016 at room temperature for 8 h. Meanwhile, a 23 wt% PVB/EtOH solution was prepared by stirring dissolving the PVB powder in EtOH at room temperature for 8 h. Subsequently, SiO₂ sol and PVB/EtOH solution were mixed with the mass ratio of 3:1 and stirred for another 4 h to obtain the electrospinning precursor solution. Following electrospinning process was performed by utilizing DXES-1 spinning equipment with an applied high voltage of 15 kV, receiving distance of 15 cm, and a constant feed rate of 1 mL h⁻¹. The as-spun composite PVB/TEOS composite nanofibers were calcined at 800 °C in a muffle furnace by gradually increasing the temperature at a heating rate of 5 °C min⁻¹ to obtain SiO₂ nanofibers.

Fabrication of SNFAs

SNFAs were prepared by freeze-drying method reported in our previous work.^[2] The procedure for the preparing of SNFA with a density of 5 mg cm⁻³ is as follows. Firstly, 1 g flexible SiO₂ nanofibers and 0.26 g SiO₂ precursor sol were uniformly dispersed in 200 g PEO solution with the content of 0.01 wt% by using high-pressure homogenizer (AH-BASIC, Shanghai Yang Yi Biotech Co., Ltd. China.). Then, the obtained fibrous dispersion was transferred to the pre-prepared molds, and frozen in liquid nitrogen bath, and then freeze-dried for 24 h to completely removing the ice crystals within the samples to obtain the unbonded polymer-assisted silica nanofibrous aerogels (PNFAs). Consequently, the PSNAs were calcined at 700 °C in a muffle furnace by gradually increasing the temperature at a heating rate of 5 °C min⁻¹ to obtain SNFAs.

Fabrication of BSAs with ultralow density of 1 mg cm⁻³

Based on the fabrication process of SNFAs above, SNFAs with a flyweight density of 0.5 mg cm⁻³ were fabricated. Subsequently, this SNFA was immersed into the pre-prepared MTMS-based silica sol with the mass content of MTMS 0.2 g. After the following hydrolysis-condensation, solvent exchange, APD, and calcination process, BSA with ultralow density of 1 mg cm⁻³ was obtained. Theoretically, the density of the aerogel obtained by this method should be 0.6 mg cm⁻³. However, the volume shrinkage of SNFA during the immersing process resulting in the increase of density.

Uncategorized References

- [1] H. Shan, X. Wang, F. Shi, J. Yan, J. Yu, B. Ding, *ACS Appl Mater Interfaces* **2017**, 9, 18966.
- [2] L. Dou, X. Zhang, X. Cheng, Z. Ma, X. Wang, Y. Si, J. Yu, B. Ding, *Acs Applied Materials & Interfaces* **2019**, 11, 29056.

Table S1. Physical properties of SNFA and BSAs.

Sample	MTMS [g]	ρ [mg cm ⁻³]	Loading of granular silica aerogel (%)	Porosity [%]	$S_{\text{BET}}^{\text{a}}$ [m ² g ⁻¹]	V_{pore} [cm ³ g ⁻¹]	$D_{\text{pore}}^{\text{b}}$ [nm]
SNFA	0	5.05	0	99.77	2.20	0.0017	34.22
BSA1	0.2	5.97	15.39	99.73	67.41	0.0472	4.10
BSA2	0.5	7.69	34.31	99.65	144.08	0.0907	3.41
BSA3	1	16.53	56.00	99.25	200.84	0.2070	5.62
BSA4	2	29.39	73.89	98.66	450.42	0.5963	6.09

^{a)} Specific surface area obtained from the nitrogen adsorption–desorption isotherms using the Brunauer-Emmett-Teller equation; ^{b)} Mean pore diameter obtained from the nitrogen adsorption–desorption isotherms according to the Barrett-Joyner-Halenda method.

Table S2. The relevant properties of BSAs and other commonly used thermal insulators

Materials	Density (mg cm ⁻³)	Thermal conductivity (W m ⁻¹ K ⁻¹)	Maximum working temperature (°C)	Compressibility
HNAs	1–30	0.022 - 0.027	1100	Superelastic
PU foams	30 – 200	0.027 – 0.2	200	Elastic
Glass fiber/SiO ₂ aerogels	50 – 300	0.04 – 0.2	800	Elastic
Nonwovens	50 – 200	0.05 – 0.3	150	Elastic

Fig. S1 – S13

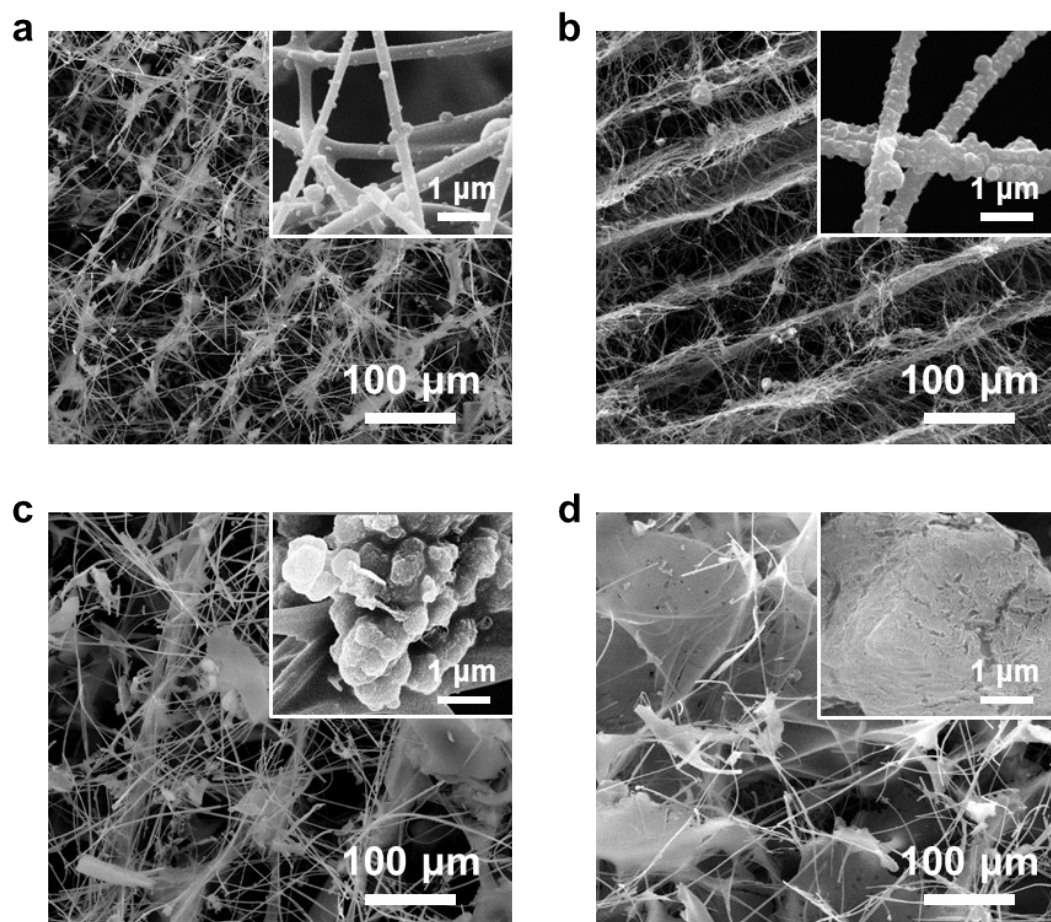


Fig. S1 SEM images of BSA1 (a), BSA2 (b), BSA3 (c) and BSA4 (d).

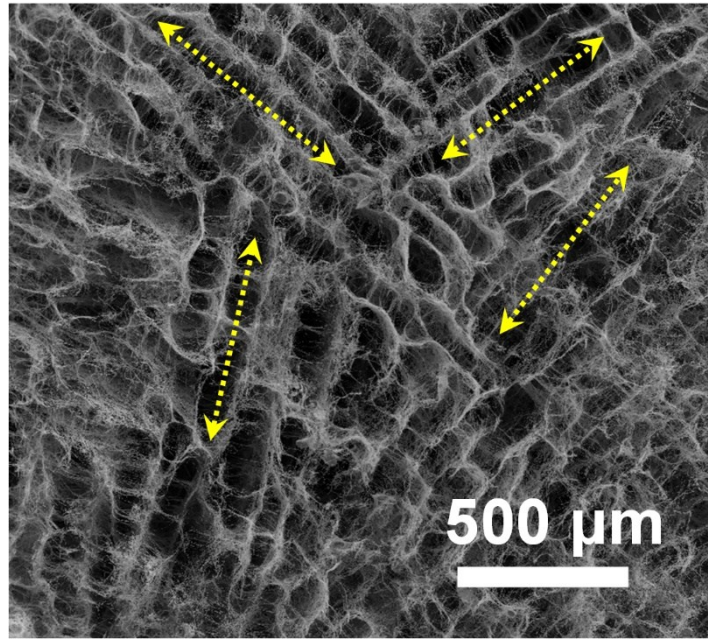


Fig. S2 Micro-orientation and macro-isotropic structure of BSAs.

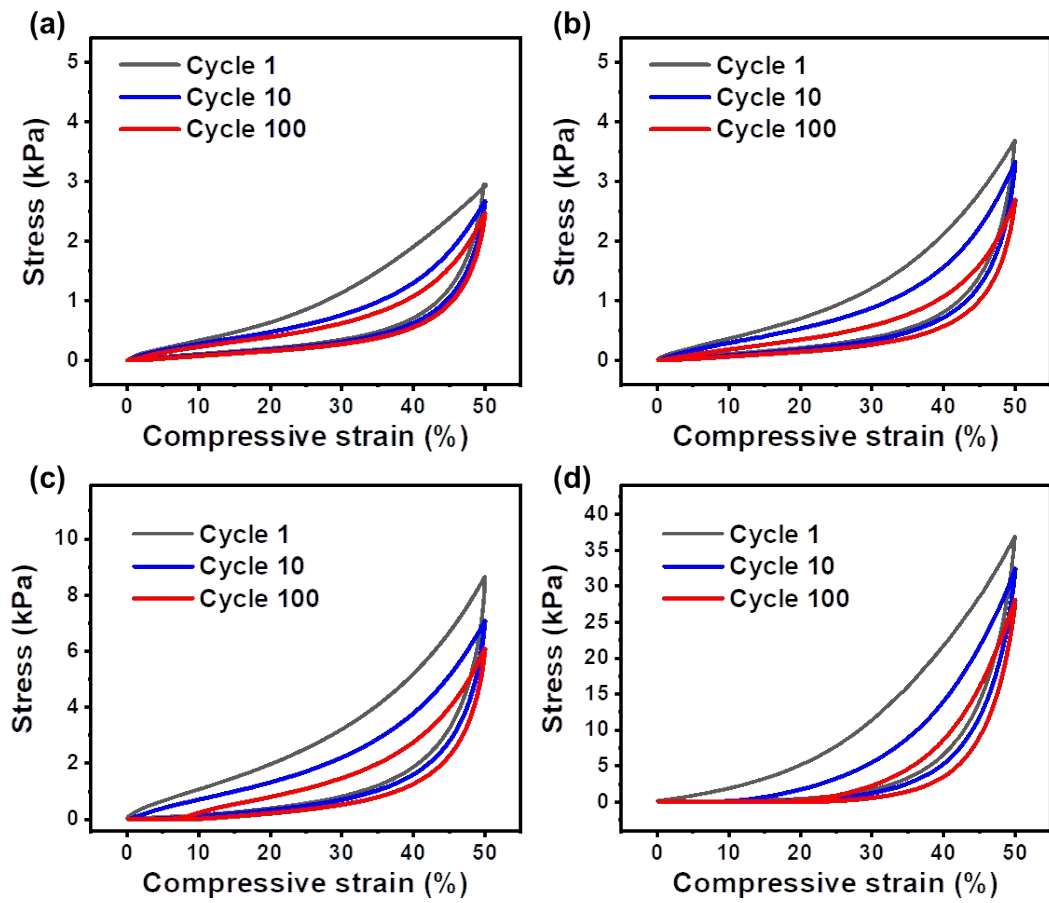


Fig. S3 100-cyclic compressive test of BSA1 (a), BSA2 (b), BSA3 (c), and BSA4 (d).

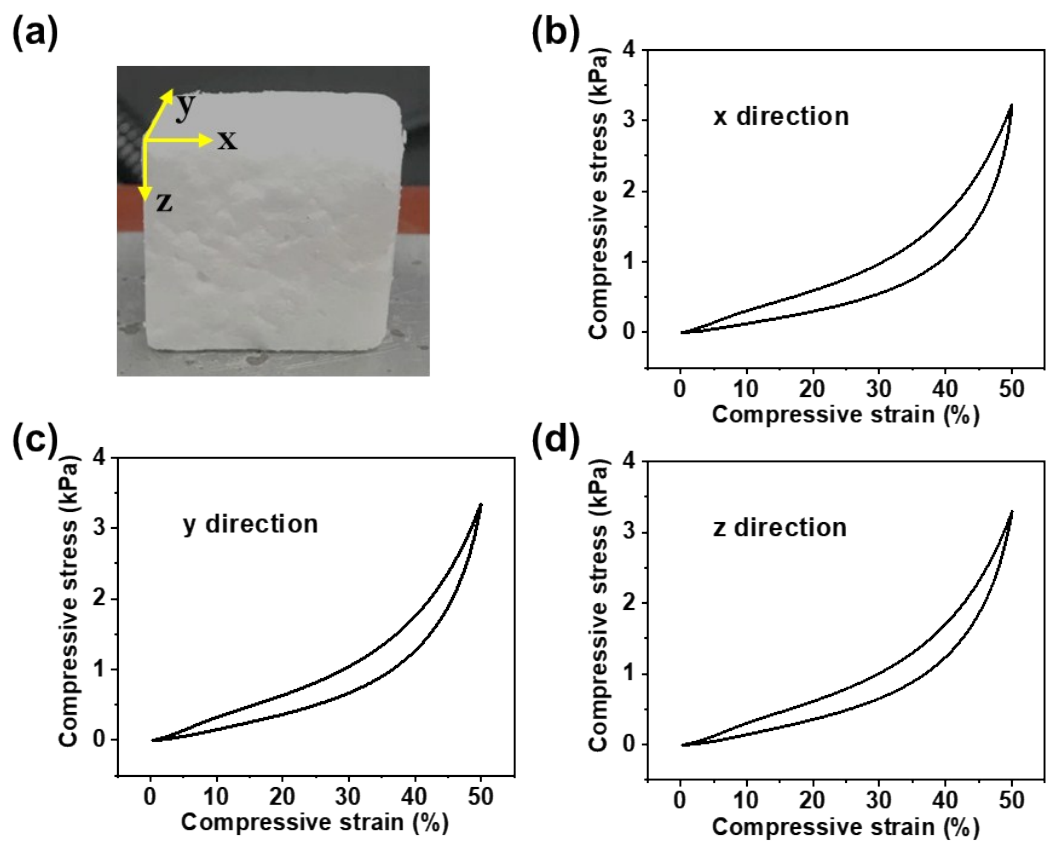


Fig. S4 (a) Three compressing direction (x, y, and z) on a cubic BSA sample. (b-d) Compressive stress versus strain curves for BSAs under three compressing direction.

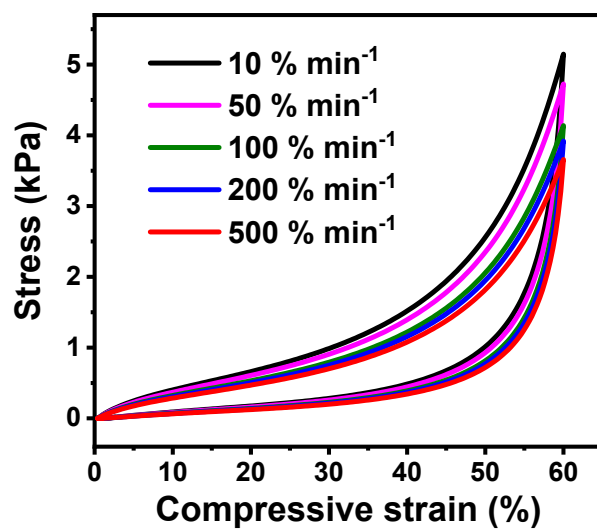


Fig. S5 The compressive σ - ϵ curves of BSAs under different compressive rates ranging from 10 to 500 mm min⁻¹.

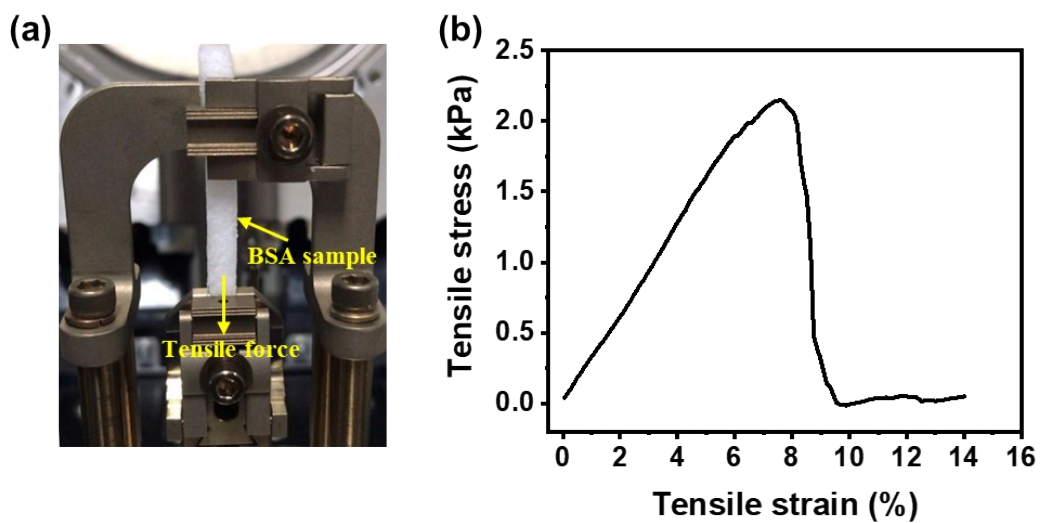


Fig. S6 (a) The measurement of tensile mechanical property was performed by using a TA-Q850 DMA instrument with a tensile clamp. (b) Tensile σ - ε curve of BSAs.

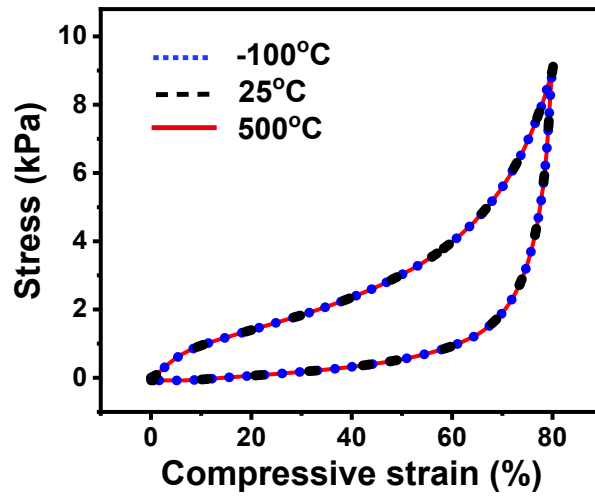


Fig. S7 The single-cycle σ - ε curve at -100°C and 500°C are almost completely the same with the curve at 25°C ($\varepsilon = 80\%$, both along the axial direction).

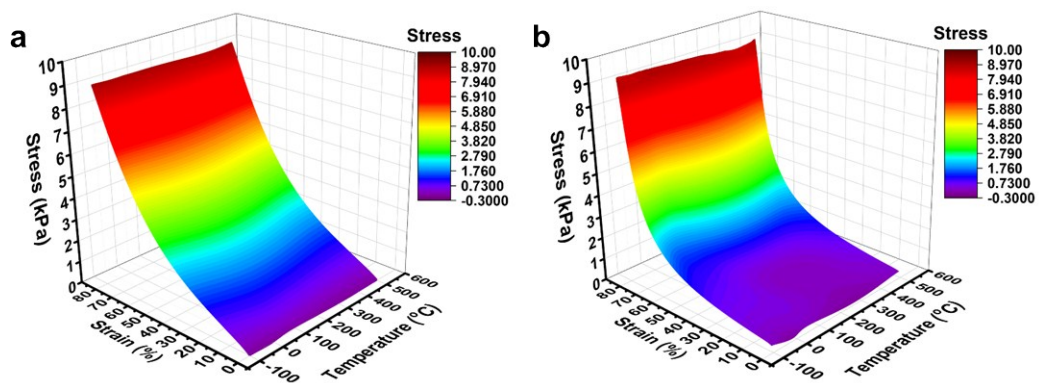


Fig. S8 3D surface graphs of the stress dependence on strain and temperature in the compression (a) and release(b) process of BSAs.

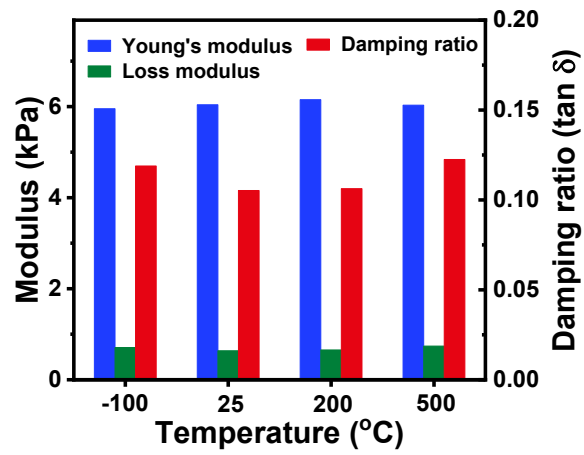


Fig. S9 The Young's modulus, loss modulus, and damping ratio for the first cycle of BSAs ($\varepsilon = 60\%$) at different temperature.

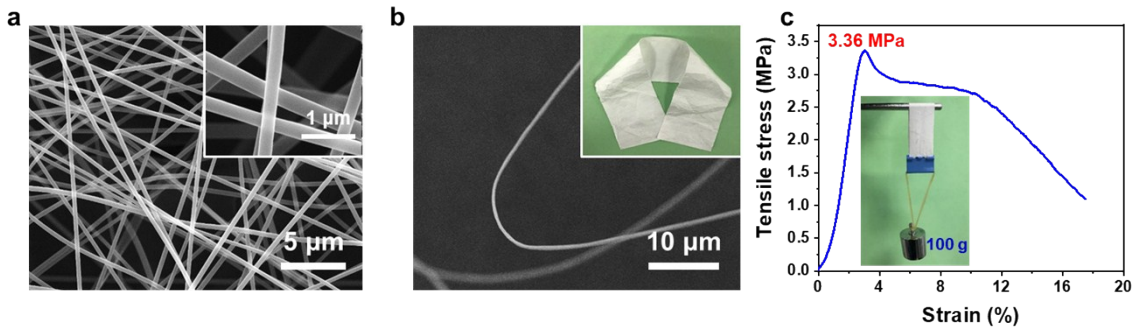


Fig. S10 **a** SEM of silica nanofibrous membrane. **b** SEM of a single nanofiber showing the good flexibility. **c** The tensile stress–strain curve of silica nanofibrous membrane. Inset: Optical photograph of silica nanofibrous membrane showing superior stretch resistance.

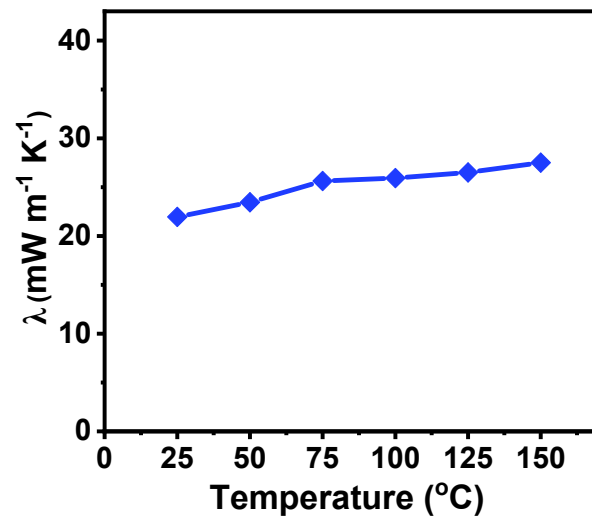


Fig. S11 The thermal conductivities of the BSA2 at different temperature.

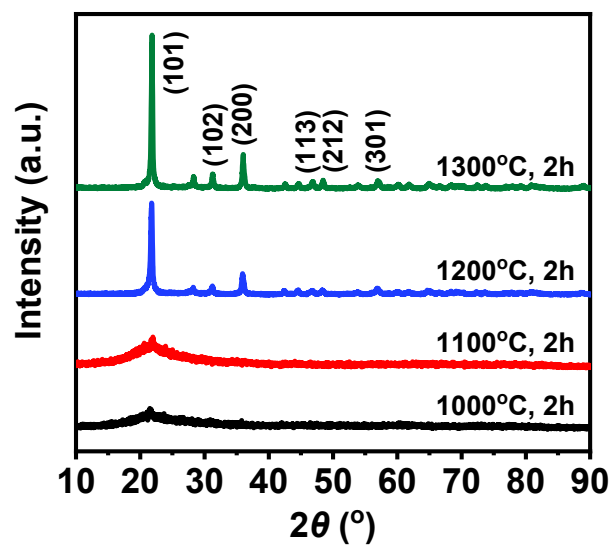


Fig. S12 XRD patterns of BSA2 after calcined at 1000, 1100, 1200 and 1300°C for 2 h.

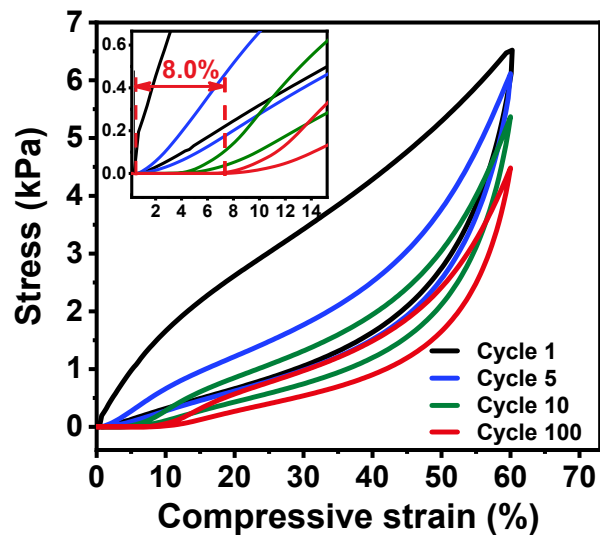


Fig. S13 100-cyclic compressive test of BSA2 after calcined at 1100°C for 2 h.