

Amorphous framework doping of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ thermoelectrics via Prussian Blue-derived phases

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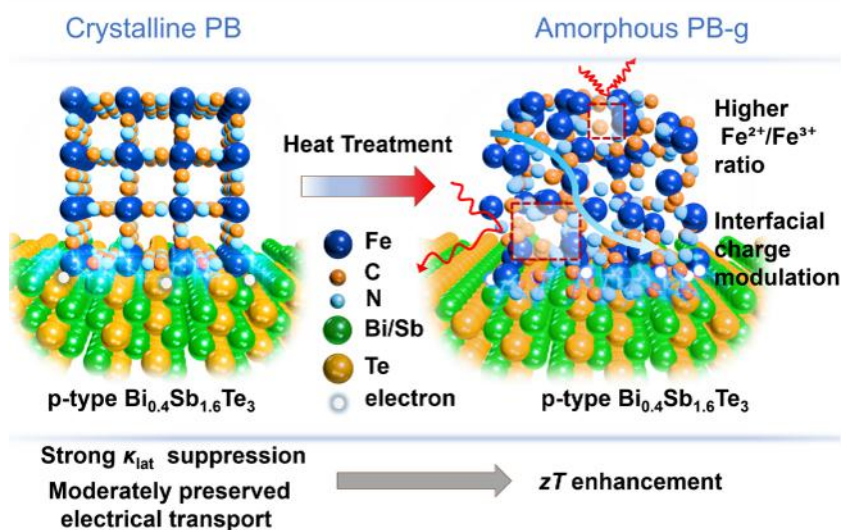
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Thermal pretreatment converts crystalline PB into PB-g domains in p-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$. The resulting structural disorder and heterogeneous interfaces introduce additional phonon-scattering channels and suppress lattice thermal conductivity, thereby improving thermoelectric performance.

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ABSTRACT: $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ (BST) is a benchmark thermoelectric material near room temperature, but further improvement in zT requires stronger suppression of lattice thermal conductivity without severely degrading electronic transport. Here, Prussian blue (PB), a cyanide-bridged coordination framework, is introduced as a structurally tunable second phase. Thermal pretreatment transforms crystalline PB into an amorphous PB-derived framework that loses long-range periodicity while retaining short-range Fe–C–N coordination, mixed Fe valence states, and mesoporosity. Compared with crystalline PB, the amorphous PB-derived phase more effectively suppresses lattice thermal conductivity through enhanced structural disorder, heterogeneous interfaces, and pore-related phonon scattering, while causing only a moderate deterioration of electronic transport. The enhanced Seebeck coefficient partly compensates for the reduced electrical conductivity, whereas the dominant contribution to the zT enhancement originates from the pronounced reduction in lattice thermal conductivity rather than from an increase in power factor. Consequently, the optimized BST/0.8 wt% 573 K PB composite achieves a peak zT of approximately 1.56 over 325–375 K, an average zT of approximately 1.27 over 300–500 K, and a measured prototype-module conversion efficiency of about 7.0% at $\Delta T = 231$ K. These results demonstrate that amorphous PB-derived framework domains provide effective broadband phonon scattering with limited degradation of electronic transport in Bi–Sb–Te thermoelectrics.

KEYWORDS: $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$; Prussian Blue; amorphous second phases; thermoelectric; zT enhancement

Introduction

Thermoelectric (TE) materials convert heat directly into electricity and offer a solid-state route for waste-heat recovery and temperature control. Their performance is quantified by the dimensionless figure of merit zT , which increases with a large Seebeck coefficient S , high electrical conductivity σ , and low thermal conductivity κ [1–4]. In practice, these transport parameters are strongly interdependent: increasing carrier concentration usually enhances σ but suppresses S , while strategies that reduce the lattice thermal conductivity κ_{lat} by introducing disorder or interfaces often introduce additional carrier scattering and degrade mobility. Decoupling charge and heat transport therefore remains a central challenge in TE materials design [1,3–6].

Near room temperature, Bi–Sb–Te alloys, particularly p -type $(\text{Bi,Sb})_2\text{Te}_3$, are among the most widely used and best-performing TE materials [7–10]. Their success stems from favorable band structures, relatively high carrier mobility, and intrinsically low lattice thermal conductivity. Over the past decades, alloying, carrier concentration tuning, and microstructure engineering have pushed the peak zT of $(\text{Bi,Sb})_2\text{Te}_3$ -based compounds close to their practical limits and enabled commercial modules [5,7,10–13]. Further improvement increasingly relies on multi-scale phonon

engineering, where point defects, grain refinement, dislocations, and second-phase inclusions are combined to scatter phonons over a broad frequency range [11–17]. Among these approaches, second-phase design is particularly attractive because a well-chosen inclusion can provide interfacial phonon scattering, energy filtering, and a chemical reservoir for carrier or band-structure tuning. However, conventional second phases such as metallic nanoparticles, oxides, carbons, and other rigid inorganic particles usually possess stiff bonding, high sound velocity, and relatively simple, less-tunable interface chemistry [14–17]. As a result, they often behave as electronically “hard” inclusions: they can require high loadings to be effective, and the resulting interfaces tend to be resistive or to introduce sizable potential barriers, which partly offset the gains from reduced κ_{lat} .

Framework-type materials offer an appealing contrast to such rigid inorganic inclusions. Coordination frameworks built from metal nodes and cyanide or organic linkers combine soft bonding, structurally complex lattices, and rich interfacial chemistry, all of which are favorable for lowering lattice thermal conductivity [18–22]. Among them, Prussian Blue (PB) and its analogues are prototypical cyanide-bridged coordination frameworks composed of transition-metal centers linked by $\text{C}\equiv\text{N}$ ligands, forming a three-dimensional

semi-organic/semi-inorganic network. PB-type frameworks often exhibit mixed-valence Fe states and chemically flexible Fe–C≡N linkages, suggesting that they may form electronically less disruptive interfaces with chalcogenide semiconductors than many rigid oxide or carbon inclusions [23–26]. Moreover, the PB lattice is structurally flexible: depending on processing conditions, it can exist as a long-range-ordered crystalline framework or as a structurally disordered, glass-like framework in which short-range Fe–C–N coordination is largely preserved while long-range periodicity is lost [27–30]. Such structural tunability opens the possibility of using the same chemistry to tune the balance between phonon scattering and electronic compatibility.

So far, the role of PB-type frameworks as structurally tunable second phases in bulk chalcogenide thermoelectrics has not been clearly established. Previous work on framework-derived additives has mainly focused on crystalline coordination phases dispersed at grain boundaries, or on mechanically amorphized MOF residues used primarily as phonon scatterers, often at relatively high loadings and without detailed control of their electronic function [19,22,27–30]. Systematic comparison between crystalline and amorphous states of a single framework chemistry in the same TE host, and understanding how framework disorder and metal valence jointly influence both κ_{lat} and the power factor $S^2\sigma$, are still limited.

In this work, BST denotes $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, and PB denotes the untreated crystalline Prussian blue precursor. Experimentally heat-treated samples are uniformly denoted x K PB, where x represents the PB pretreatment temperature before composite preparation. This processing-based designation identifies the pretreatment condition and does not imply that the treated sample remains crystalline. The actual structural state of each sample is determined from the corresponding structural and spectroscopic characterization. PB-g denotes the amorphous or glassy PB-derived framework that lacks long-range order while retaining local Fe–C–N coordination. It is used as a structural descriptor and for the periodic disordered-supercell model in the computational discussion, rather than as the name of a specific experimental sample. Composite samples are written as BST/ y wt% x K PB, where y is the PB-derived-phase loading. The 10 wt% composites are structural/spectroscopic model samples used to enhance weak framework-related signals, whereas BST/0.8 wt% 573 K PB is the transport-optimized composite and the p -type leg

material used in the thermoelectric module.

By comparing pristine BST, crystalline-PB-modified BST, and amorphous-PB-modified BST, we show that both framework states introduce additional interface-driven phonon scattering, whereas the amorphous PB-derived phase produces a stronger reduction in κ_{lat} because of its greater structural disorder, higher effective interface density, and pore-related features. The amorphous phase does not form an extended conductive pathway. Instead, the transport data are consistent with local interfacial charge redistribution, partial carrier compensation, and energy-dependent carrier scattering. This combination enhances S , moderately preserves the power factor, and strongly suppresses κ_{lat} , thereby broadening the high- zT temperature window.

Results and Discussion

The overall design concept of the PB- $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ composites is summarized schematically in Fig. 1. Prussian-blue-derived frameworks are introduced as structurally tunable secondary phases that can simultaneously influence carrier transport and phonon scattering at the nano- and microstructural levels [14–17,22]. In the crystalline state, PB retains a relatively ordered Fe–C–N framework and forms discrete heterointerfaces with the p -type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ matrix. Such crystalline domains can contribute interfacial phonon scattering, but their relatively ordered lattice and limited structural disorder provide a comparatively modest reduction in κ_{lat} . Meanwhile, the interfaces also introduce additional carrier scattering, so the net transport benefit remains limited.

Upon amorphization, the PB-derived framework becomes more structurally disordered and vacancy-rich, which strengthens phonon scattering and is expected to lower κ_{lat} more effectively. At the same time, the amorphous framework remains electronically relevant at the heterointerface, not by acting as a bulk conductive phase, but by modifying the local interfacial electronic environment. The increased $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio observed after thermal treatment suggests a larger population of electron-rich interfacial sites, which can contribute to partial carrier compensation and interfacial charge redistribution in the p -type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ matrix [23–26]. Together with the increased interface density, these features are expected to improve the balance between suppressed lattice thermal conductivity and preserved charge transport across the composite. This design concept is examined experimentally and computationally in the following sections.

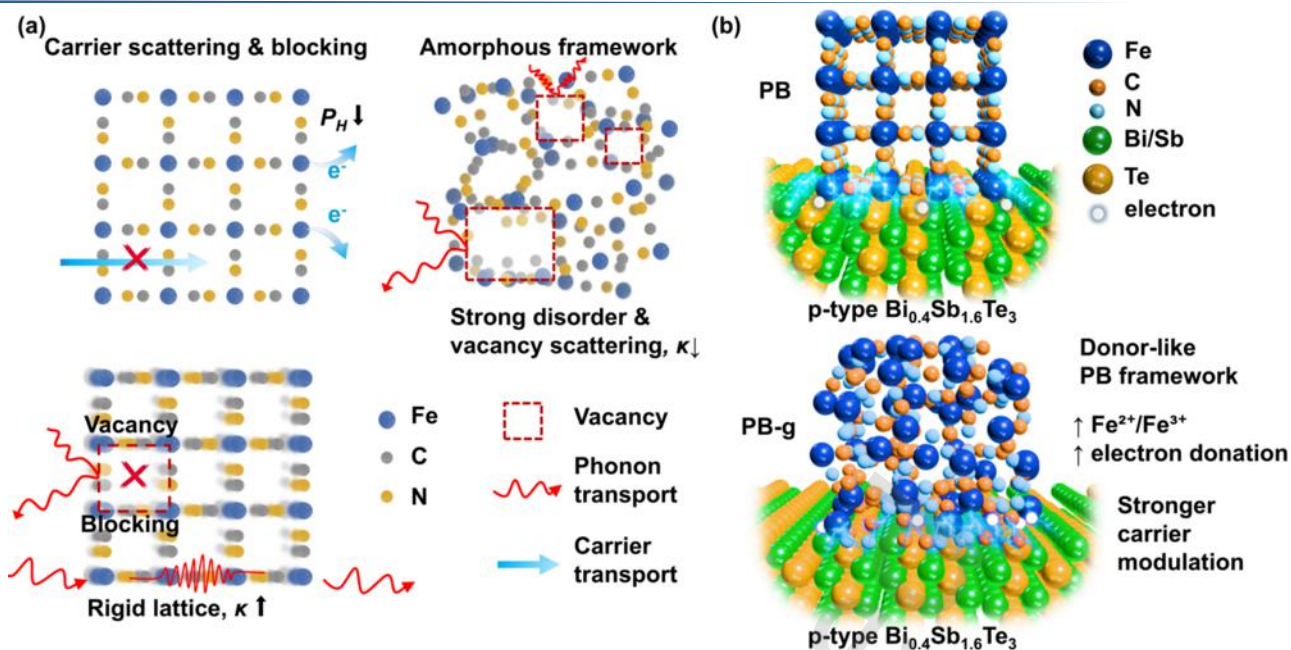


Figure 1. Schematic illustration of the proposed roles of crystalline PB and amorphous PB-g in *p*-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ (BST) composites. (a) Crystalline PB introduces interfacial carrier scattering and local transport blocking but provides relatively limited phonon scattering, whereas the more disordered and vacancy-rich PB-g enhances phonon scattering and more effectively suppresses the lattice thermal conductivity, κ_{lat} . (b) The increased $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and disordered PB-g/BST interfacial environment may promote interfacial charge redistribution and carrier modulation while preserving the continuity of charge transport through the BST matrix.

To establish the crystalline/amorphous structural contrast, TEM and STEM-EDS analyses were first performed on BST/10 wt% pristine PB and BST/10 wt% 573 K PB structural/spectroscopic model composites (Fig. 2). The high loading was selected to strengthen the weak framework-related contrast and Fe/C/N signals. The 10 wt% specimens are not assumed to reproduce the number density or spatial distribution of PB-derived domains in the optimized 0.8 wt% transport composite. In the crystalline model composite, the PB-rich region displays resolvable lattice fringes and a spot-like SAED pattern, whereas the thermally pretreated PB-derived region shows disordered contrast and a diffuse diffraction feature. These observations support a crystalline-to-amorphous transformation of the framework-derived phase.

The STEM-EDS maps in Fig. 2 show a Bi/Sb/Te-rich BST matrix together with spatially diffuse Fe, C, and N signals. Because STEM-EDS integrates signals through the TEM-foil thickness, PB-derived species located at surfaces, interfaces, or overlapping regions may be projected onto the BST matrix. The elemental maps are therefore not used as stand-alone evidence for a sharply separated BST/PB-derived-phase boundary. Fe is treated as the primary compositional indication of PB-derived species, whereas the weaker C and N signals are used only as auxiliary information.

Additional particle-morphology comparisons across the processing stages are provided in Figs. S1, S2, and S3 in the ESM. The representative SAED/TEM results in Figure S1 indicate that the 573 K pretreatment causes the loss of long-range order without obvious growth or large-scale coalescence of the PB precursor particles. The SEM

comparison in Figure S2 suggests that the nanoscale particulate features observed after SPS are slightly larger than the pristine PB particles, indicating limited coalescence or growth during consolidation. Figure S3 further shows that decreasing the PB loading from 10 wt% to 0.8 wt% mainly reduces the abundance of the particulate features, while their overall apparent size range remains broadly similar. The optimized composite retains a continuous plate-like BST grain framework with sparse particulate features, occasional intergranular voids, and no obvious large-scale aggregation. Because these observations are based on representative TEM and SEM images, no quantitative particle-size distribution is inferred. In addition, the particulate features are described morphologically because SEM contrast alone cannot establish their chemical identity.

Direct post-SPS TEM/HRTEM/FFT/STEM-EDS characterization of the actual BST/0.8 wt% 573 K PB transport composite is provided in Figure S4. HRTEM and FFT analyses identify crystalline BST regions adjacent to regions with disordered contrast. STEM-EDS maps acquired from another representative area of the same specimen show weak but detectable Fe signals together with auxiliary C and N signals. The disordered contrast is therefore tentatively associated with an amorphous PB-derived region based on the combined structural and specimen-level compositional evidence. Because the HRTEM and STEM-EDS data were acquired from different representative regions, no one-to-one spatial correlation is claimed. Density and relative-density data in Table S1 provide complementary information on bulk densification and residual porosity.

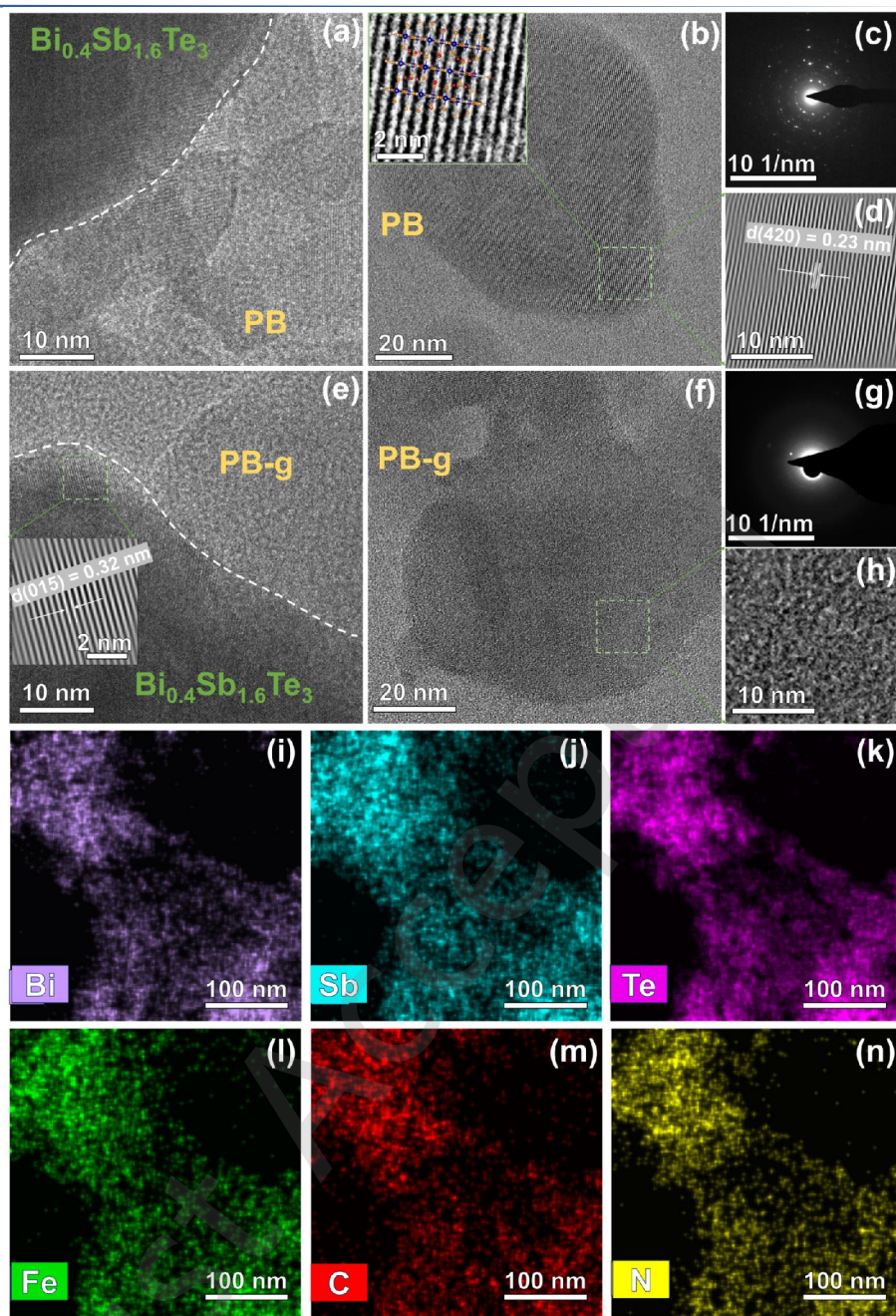


Figure 2. TEM characterization of the BST/10 wt% PB structural/spectroscopic model composites. (a–d) BST/10 wt% pristine PB, showing a crystalline PB-derived region (legacy PB label in the image) with lattice fringes and spot-like diffraction. (e–h) BST/10 wt% 573 K PB, showing an amorphous PB-derived region (legacy PB-g label in the image) with disordered contrast and diffuse diffraction. (i–n) STEM-EDS maps of Bi, Sb, Te, Fe, C, and N. The diffuse Fe/C/N signals are interpreted together with HRTEM/SAED and are not used alone to define a sharp phase boundary. Direct microscopy of the transport-optimized BST/0.8 wt% 573 K PB composite is provided in Figures S3 and S4 in the ESM.

To clarify the intrinsic structural evolution of the PB-derived framework, the characterization results of the isolated PB samples are discussed separately in this section. Pristine PB exhibits long-range crystalline order, whereas thermal pretreatment progressively weakens long-range periodicity and produces an amorphous PB-derived framework. Although long-range order is largely lost, local Fe–C–N coordination and pore-related structural features are partially retained. The XRD, FTIR, Raman, PDF, electron-diffraction, and N_2 adsorption results are therefore considered together to establish the crystalline-to-amorphous structural evolution. In Fig. 3, pristine PB shows

sharp framework reflections, while the peaks progressively broaden and weaken until a diffuse background dominates at 573 K. The FTIR bands assigned to Fe–C and $C\equiv N$ broaden and decrease in intensity, and features in the $1300\text{--}1500\text{ cm}^{-1}$ region are tentatively assigned to C–N/C=N-containing fragments formed by partial rearrangement of the cyanide-linked framework [31]. Room-temperature Raman spectra provide supplementary support for this structural evolution. Compared with pristine PB, the 573 K PB spectrum exhibits broader and less-resolved framework-related features in the $200\text{--}600\text{ cm}^{-1}$ region, consistent with increased local structural disorder after thermal pretreatment (Figure S5).

The total pair distribution functions $G(r)$ provide complementary evidence for this crystalline-to-amorphous evolution. Pristine PB shows well-resolved correlations extending beyond 15 Å. With increasing pretreatment temperature, the medium- and long-range peaks are strongly damped, whereas the first few low- r correlations remain visible. The retained short-range N-C, C-N, and Fe-C/N correlations demonstrate that the primary local coordination motif survives despite the loss of long-range periodicity [23,24].

The enlarged low- r region further reveals how the local structural changes induced in the isolated PB-derived phases are carried into the BST composites. As highlighted by the red dashed circles in Figure 3e, thermal pretreatment produces pronounced changes in the peak shape and intensity within the approximately 3.2–3.7 and 4.5–5.0 Å regions, reflecting rearrangement of local and intermediate-range atomic correlations in the PB framework. Importantly, corresponding differences remain visible at similar r positions when the BST/10 wt% pristine PB and BST/10 wt% 573 K PB model composites are compared in Figure 3f. Because the two composites contain the same BST matrix, these residual differences are attributed primarily to the

different local structural states of the incorporated PB-derived phases. The results therefore indicate that the local structural fingerprints generated by PB amorphization are not erased during composite preparation and SPS consolidation, but are at least partially retained after incorporation into BST. The composite PDF data are used as supporting evidence for the preservation of PB-derived local structural differences rather than as proof that the complete PB framework remains unchanged.

Overall, the isolated-phase measurements establish the intrinsic structural evolution before the composite-specific interfacial evidence is considered. Complementary SAED and bright-field TEM observations in Figure S1 show a diffuse halo after the 573 K pretreatment while the aggregated nanoparticle morphology is broadly retained, indicating amorphization without obvious large-scale coalescence or particle coarsening.

Thermogravimetric analysis further shows that the BST-containing composites undergo substantially smaller mass loss than the isolated PB-derived powders over the measured temperature range, supporting their thermal robustness within the relevant processing and operating-temperature window (Figure S6).

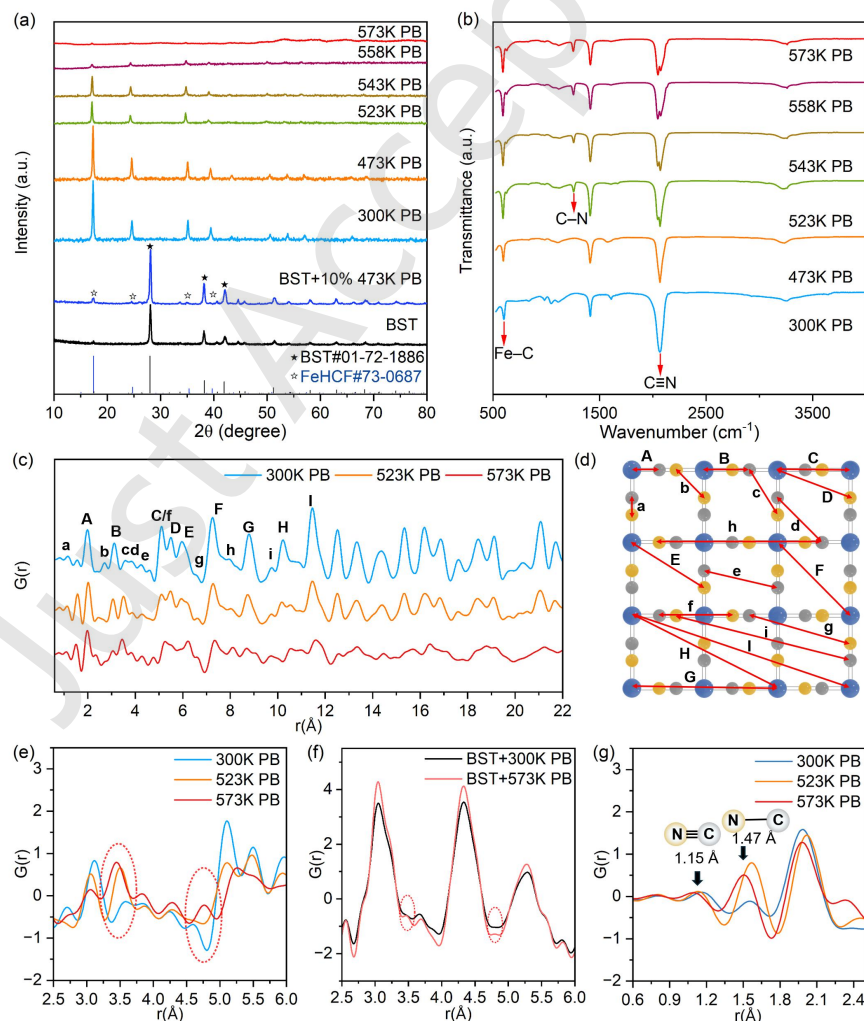


Figure 3. Structural evolution from pristine crystalline PB to progressively amorphized PB-derived framework phases, together with explicitly identified BST reference data. (a) XRD patterns of pristine PB (300 K PB), PB thermally pretreated at 473–573 K, pristine BST, and the BST/10 wt% 473 K PB structural model composite. (b) FTIR spectra of pristine and thermally pretreated PB, highlighting Fe-C, C≡N, and emergent C-N/C=N-related features. (c) Total pair distribution functions $G(r)$ of isolated PB at 300, 523, and 573 K. (d) Schematic PB framework showing representative Fe-Fe correlations assigned to peaks in (c). (e) Enlarged 2.5–6 Å region highlighting the temperature-dependent changes in selected local- and intermediate-range atomic correlations. (f) Enlarged 2.5–6 Å region highlighting the temperature-dependent changes in selected local- and intermediate-range atomic correlations. (g) Enlarged 0.6–2.4 Å region highlighting the temperature-dependent changes in selected local- and intermediate-range atomic correlations.

intermediate-range correlations of the isolated PB-derived phases; the red dashed circles mark the regions showing the most evident structural evolution. (f) $G(r)$ comparison of the BST/10 wt% pristine PB and BST/10 wt% 573 K PB structural/spectroscopic model composites. The differences retained at corresponding r positions indicate that the local structural fingerprints associated with PB amorphization remain partially preserved after incorporation into BST and SPS consolidation. (g) Enlarged low- r region showing the representative short-range N-C and C-N correlations retained in the isolated PB-derived phases after thermal pretreatment.

The textural evolution of the isolated PB-derived phases was first examined by N_2 adsorption-desorption measurements (Fig. 4(a),(b)). Pristine PB and the thermally pretreated PB samples exhibit pronounced mesoporous characteristics, whereas the dense BST reference shows little resolvable pore volume within the measured mesopore range. After thermal pretreatment, the pore-size distribution of PB becomes broader and extends toward larger pore diameters, indicating the development of a more heterogeneous pore architecture. This evolution is consistent with partial cleavage, local collapse, and structural rearrangement of the cyanide-linked framework, which may generate voids and framework domains with a wider range of characteristic dimensions. After incorporation into BST, these multiscale pore-related features can provide additional scattering centers for phonons with different wavelengths and mean free paths. In addition, differences in bonding stiffness and vibrational characteristics among crystalline BST, disordered PB-derived domains, and pore-related interfaces may enhance interfacial vibrational mismatch and thereby contribute to the suppression of lattice thermal conductivity [11–17,22]. Because the adsorption measurements were performed on isolated PB-derived powders, they describe the intrinsic textural evolution of the framework and do not directly quantify the pore volume retained in the SPS-consolidated composites. The densification of the bulk specimens is evaluated separately using the density and relative-density data in Table S1.

The Fe 2p XPS spectra further reveal changes in the local Fe electronic state during thermal pretreatment (Fig. 4(c),(d)). Both pristine PB and 573 K PB retain mixed Fe(II)/Fe(III) character [23–26]. Within the adopted peak-fitting model, the fitted Fe^{2+}/Fe^{3+} proportion increases from approximately 47:53 in pristine PB to 75:25 after treatment at 573 K. This increase in the Fe^{2+} contribution suggests the formation of a more reduced and electron-rich local Fe environment and is consistent with partial cleavage and rearrangement of Fe-C $\equiv$ N-Fe linkages during framework amorphization [31]. The accompanying structural reconstruction may increase the population of terminal, defect-associated, or under-coordinated Fe sites. Thermal pretreatment therefore modifies not only the long-range framework order but also the local electronic environment of the Fe centers, producing a larger population of potentially electron-donating Fe^{2+} sites.

To examine how the Fe-centered electronic and coordination environments change upon composite formation, Fe K-edge XANES and EXAFS measurements were performed on isolated 573 K PB and the corresponding BST/10 wt% 573 K PB structural/spectroscopic model composite after SPS consolidation (Fig. 4(e),(f)). Relative to isolated 573 K PB, the composite exhibits a slight shift of the Fe absorption edge toward higher energy, together with a variation in the 1s $\rightarrow$ 3d pre-edge feature. These changes are consistent with a modest increase in the average Fe oxidation state and modification of the local coordination symmetry, although

structural disorder and coordination reconstruction may also contribute to the spectral differences. The spectra therefore indicate modification of the Fe-centered electronic and coordination environment after incorporation into BST, rather than serving as stand-alone proof of a unique interfacial charge-transfer pathway.

The k^3 -weighted Fourier-transformed Fe K-edge EXAFS spectra in Fig. 4(f) retain detectable Fe-centered short-range correlations after incorporation into BST. However, changes in peak amplitudes, positions, and line shapes indicate reconstruction and increased disorder of the local Fe coordination environment. These results suggest that characteristic short-range Fe-C/N and Fe-Fe correlations remain after composite preparation and SPS consolidation, rather than the PB-derived phase undergoing complete decomposition.

Representative PB/BST interface models were further examined using charge-density-difference calculations (Fig. S7). Both Fe^{3+} - and Fe^{2+} -centered local configurations exhibit localized interfacial charge redistribution, whereas the Fe^{2+} -containing model shows a larger calculated charge-transfer magnitude than the Fe^{3+} -containing model. These calculations qualitatively support a stronger donor-like interfacial response from Fe^{2+} -rich PB-derived regions. However, the calculated charge-transfer values depend on the selected interface models and are not interpreted as evidence for a unique atomically resolved transfer pathway in the experimental composite.

Complementary Bi K-edge, Sb K-edge, and Te K-edge XANES and Fourier-transformed EXAFS spectra of pristine BST and the BST/10 wt% 573 K PB structural/spectroscopic model composite are provided in Fig. S8 in the ESM. The principal local coordination features of the BST matrix are retained after incorporation of the PB-derived phase, whereas subtle changes in the EXAFS peak intensities and line shapes and in the XANES absorption-edge profiles are consistent with local coordination distortion and interfacial electronic perturbation.

Taken together, the XPS, XANES, EXAFS, and charge-density-difference results are consistent with a plausible mechanism in which thermal pretreatment produces a structurally disordered and Fe^{2+} -enriched PB-derived framework. After incorporation into BST, the electron-rich Fe sites participate in localized interfacial charge redistribution and may exhibit donor-like behavior toward the p -type matrix. This localized electronic perturbation provides a plausible origin for the carrier modulation observed in the PB-modified BST composites, while the structurally disordered and porous framework simultaneously strengthens phonon scattering. Such interface-mediated carrier regulation is conceptually related to modulation-doping strategies previously reported for thermoelectric heterostructures [32]. The combined evidence does not define a unique atomically resolved charge-transfer pathway.

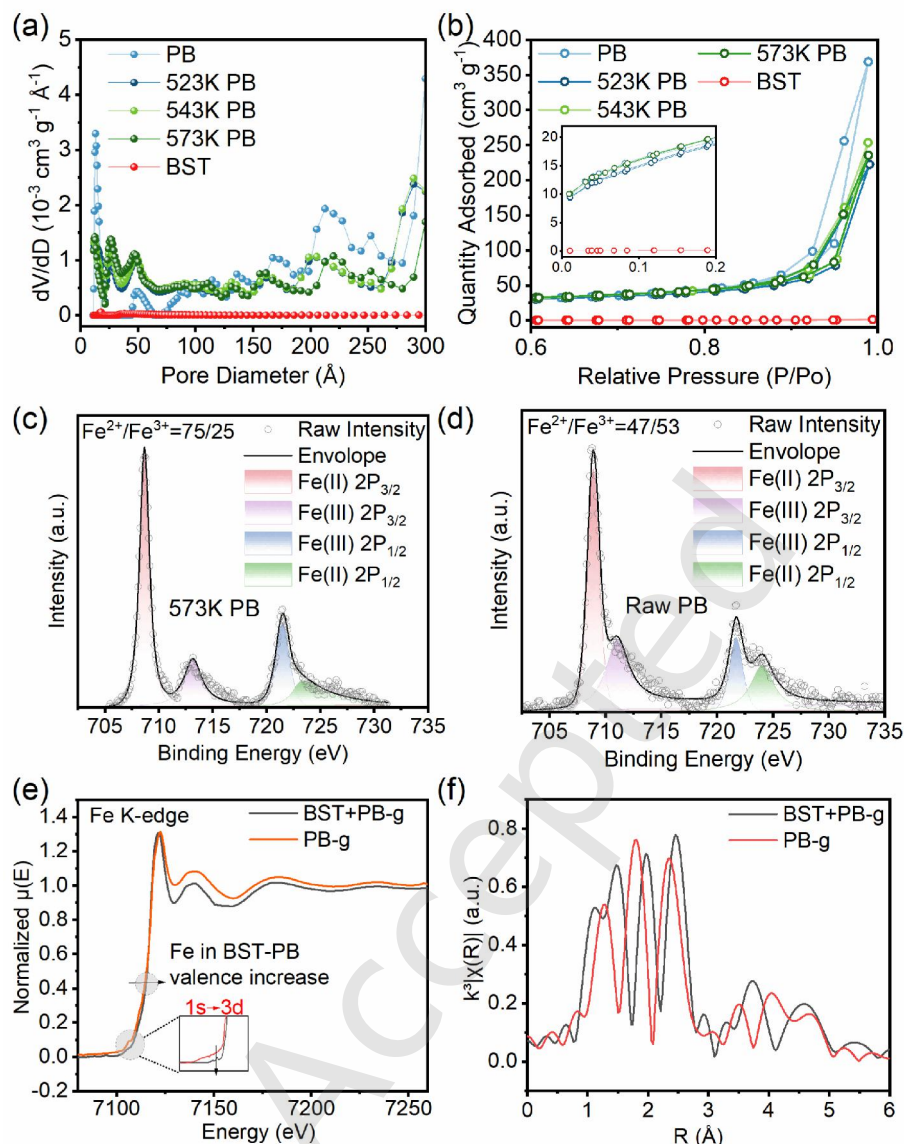


Figure 4. Textural and Fe-centered chemical evolution of isolated PB-derived phases and the BST/10 wt% 573 K PB structural/spectroscopic model composite. (a) Pore-size distributions and (b) N_2 adsorption-desorption isotherms of isolated pristine crystalline PB, PB thermally pretreated at 523, 543, and 573 K, and a dense BST reference. Thermal pretreatment broadens the mesopore-size distribution, with 573 K PB representing the strongly amorphized PB-derived state. (c,d) Fe 2p XPS spectra of strongly amorphized 573 K PB and pristine crystalline PB, showing an increase in the fitted Fe^{2+}/Fe^{3+} proportion from 47:53 to 75:25. (e) Fe K-edge XANES and (f) k^3 -weighted Fourier-transformed EXAFS spectra of isolated 573 K PB and the corresponding BST/10 wt% 573 K PB structural/spectroscopic model composite after SPS consolidation. The slight absorption-edge shift and changes in the EXAFS line shape are consistent with modification of the average Fe electronic state and reconstruction of the local Fe coordination environment in the composite. In panels (e,f), the legacy labels “PB-g” and “BST+PB-g” denote isolated 573 K PB and BST/10 wt% 573 K PB, respectively.

To compare the intrinsic electronic and vibrational characteristics of crystalline PB and PB-g, calculations were performed using the crystalline PB structure and a periodic disordered supercell representing PB-g (Fig. 5). As shown in Fig. 5(a–c), PB-g exhibits more congested and less dispersive low-frequency vibrational features than crystalline PB, together with lower phonon group velocities in the frequency range most relevant to lattice heat transport. These characteristics indicate enhanced vibrational localization and more pronounced phonon-glass-like behavior in PB-g.

The phonon densities of states in Figure 5f show that both PB and PB-g exhibit pronounced spectral mismatch with BST over broad frequency ranges. Such vibrational incompatibility can impede phonon transmission across the PB/BST and PB-g/BST interfaces, increase the interfacial thermal resistance, and thereby enhance interfacial phonon

scattering [14–17,22]. In addition, the greater structural disorder, flatter vibrational branches, lower group velocities, and stronger mode localization of PB-g further suppress the propagation of heat-carrying phonons. The isolated high-frequency $C\equiv N$ stretching modes near 60–70 THz lie far above the principal vibrational range of BST and therefore contribute little directly to heat conduction in the matrix.

The calculated electronic structures in Fig. 5(d),(e) show PBE band gaps of approximately 2.1 eV for crystalline PB and 1.5 eV for PB-g. The smaller calculated band gap of PB-g suggests that its localized electronic states can respond more readily to the electronic environment of the BST matrix, thereby favoring local electronic polarization and interfacial charge redistribution. PB-g may therefore possess a stronger carrier-modulation capability than crystalline PB. This interpretation is consistent with the experimentally observed increase in the Fe^{2+} fraction after thermal

treatment and with the composite-induced changes in the Fe K-edge spectra, which collectively support localized donor-like interfacial charge redistribution without defining a unique transfer pathway.

At the same time, the relatively flat bands near the band edges indicate strong electronic localization, showing that neither PB nor PB-g forms an extended conductive pathway through BST. Their electronic influence is therefore mainly associated with localized interfacial charge redistribution, partial hole compensation, and energy-dependent carrier

scattering rather than bulk electrical conduction.

Taken together, the calculations suggest that PB-g combines a stronger local electronic response with lower phonon group velocities, enhanced vibrational localization, and substantial vibrational mismatch with BST. These characteristics are consistent with more effective interfacial carrier modulation, increased interfacial thermal resistance, and stronger suppression of lattice heat transport in PB-g-modified BST.

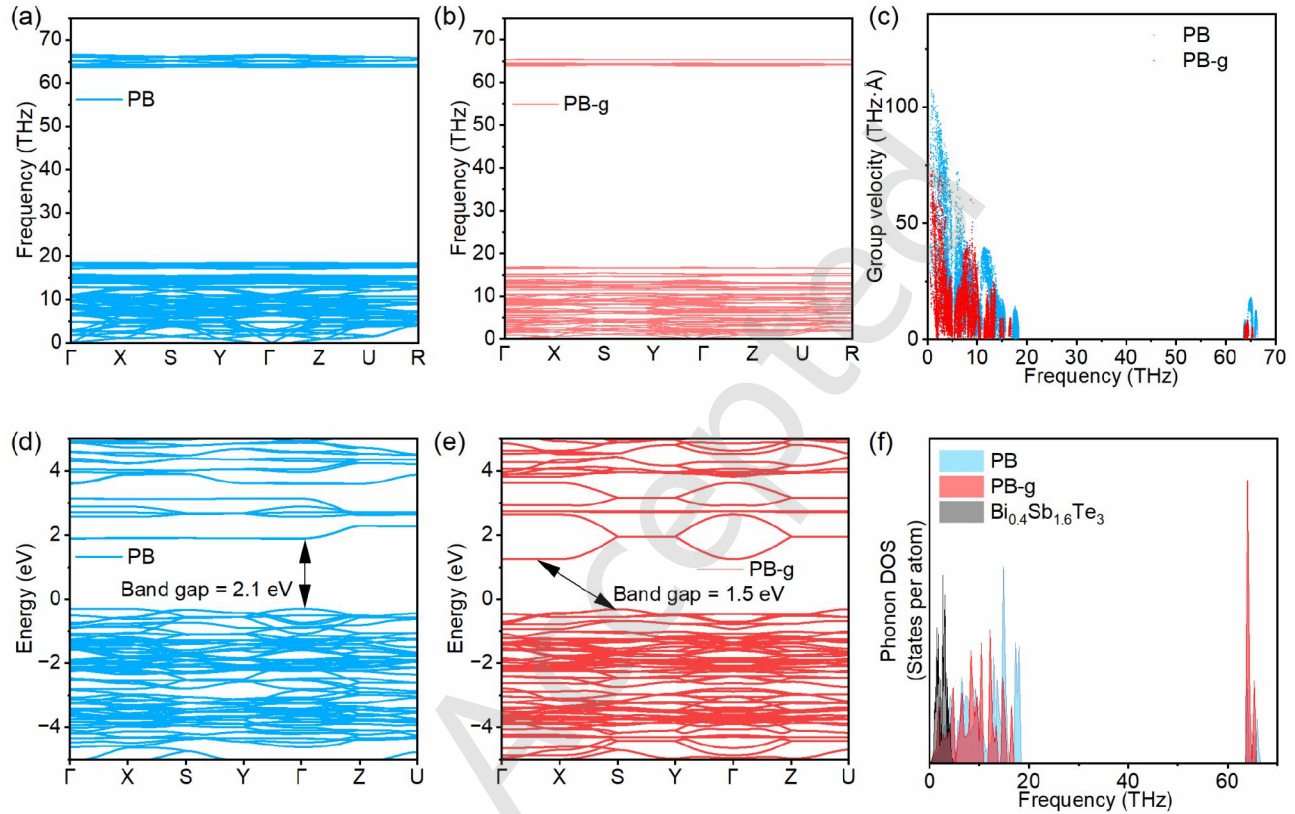


Figure 5. Calculated vibrational and electronic characteristics of crystalline PB and PB-g. (a,b) Phonon dispersion of crystalline PB and the dispersion-like representation of PB-g calculated using a periodic disordered-supercell model. (c) Phonon group-velocity magnitudes of crystalline PB and PB-g. (d,e) Calculated electronic structures of crystalline PB and the PB-g disordered-supercell model, showing PBE band gaps of approximately 2.1 and 1.5 eV, respectively. (f) Atom-normalized phonon densities of states of crystalline PB, PB-g, and Bi_{0.4}Sb_{1.6}Te₃, showing partial spectral overlap in the low-frequency region.

PB incorporation increases the Seebeck coefficient over most of the measured temperature range (Fig. 6(b)), partially compensating for the reduction in electrical conductivity. Nevertheless, pristine BST retains the highest power factor throughout the measured temperature range (Fig. 6(c)). Therefore, the enhanced zT of the PB-modified samples does not originate from a power-factor enhancement but primarily from the pronounced suppression of lattice thermal conductivity.

The Pisarenko comparison in Fig. 6(f) shows that pristine BST lies close to the $r=-0.5$ SPB baseline, whereas the PB-modified samples shift toward the $r=-0.25$ trend as the hole concentration decreases. This behavior suggests that the Seebeck enhancement is associated not only with partial carrier compensation but also with a change in the effective energy dependence of carrier scattering. Because most of the experimental points remain close to the SPB reference curves, however, the Pisarenko plot alone is not regarded as

definitive evidence for substantial modification of the electronic density of states. The comparatively moderate variation in weighted mobility is also consistent with preservation of the continuous electronic-transport network of the BST matrix [33,34].

The total thermal conductivities of all PB-modified composites are lower than that of pristine BST throughout the measured temperature range (Fig. 6(g)). Their lattice thermal conductivities are substantially reduced in the low- and intermediate-temperature regions, with BST/0.8 wt% 573 K PB exhibiting the strongest and most persistent suppression (Fig. S9). At 300 K, κ_{lat} decreases from approximately 0.7 W m⁻¹ K⁻¹ for pristine BST to approximately 0.35–0.45 W m⁻¹ K⁻¹ for the PB-containing samples. This reduction is consistent with the combined contributions of framework disorder, heterogeneous PB-derived interfaces, and pore-related phonon-scattering features.

The Debye–Callaway analysis in Fig. 6(h) is used as a semiquantitative comparison of effective phonon-scattering channels rather than as a unique inversion of microscopic structural parameters [35]. The qualitative κ_{lat} behavior of pristine BST is reproduced using intrinsic phonon–phonon, point-defect, and grain-boundary scattering terms. In contrast, the substantially lower κ_{lat} of BST/0.8 wt% 573 K PB is reproduced by additionally incorporating effective second-phase/interface and nanopore-related scattering terms. The corresponding length-scale parameters are effective values selected with reference to the microscopy and porosity observations and should not be interpreted as uniquely determined particle- or pore-size distributions.

The schematic cumulative κ_{lat} analysis in Fig. 6(i) illustrates the complementary frequency ranges covered by the different scattering mechanisms. Grain boundaries predominantly scatter low-frequency, long-wavelength phonons; PB-derived second phases and pore-related features extend the scattering into the low- and intermediate-frequency regions; and point defects become increasingly important at higher frequencies. The combined action of these mechanisms is therefore consistent with broadband phonon damping [11–17,35].

Consequently, BST/0.8 wt% 573 K PB achieves the most

favorable balance between moderately preserved electrical transport and strongly suppressed lattice thermal conductivity, reaching a peak zT of approximately 1.56 within the 325–375 K range. The dominant contribution to the zT enhancement is the pronounced suppression of κ_{lat} . The enhanced Seebeck coefficient partially compensates for the reduction in electrical conductivity and helps preserve a moderate power factor, but it does not produce a net power-factor enhancement. Repeated measurements of the optimized BST/0.8 wt% 573 K PB specimen show closely overlapping temperature-dependent thermoelectric properties, confirming good measurement repeatability (Figs. S10 and S11).

To further evaluate thermoelectric performance over the working-temperature interval, the average zT values were calculated over 300–500 K by integrating the experimentally measured $zT(T)$ curves. The resulting zT_{avg} values are approximately 1.01, 1.19, 1.10, and 1.27 for pristine BST, BST/0.8 wt% 423 K PB, BST/0.8 wt% 523 K PB, and BST/0.8 wt% 573 K PB, respectively. Thus, BST/0.8 wt% 573 K PB exhibits both the highest peak zT and the highest working-temperature-averaged zT among the investigated samples (Table S4).

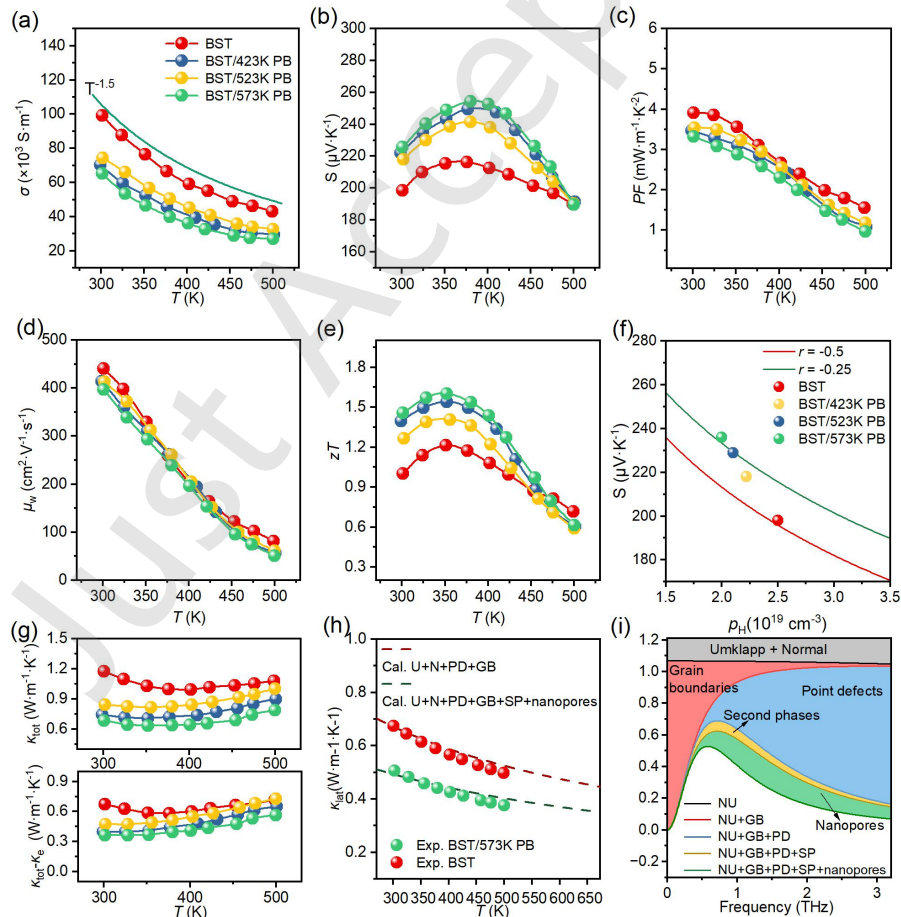


Figure 6. Thermoelectric transport properties and thermal conductivity of pristine BST and BST/0.8 wt% x K PB transport composites, where x denotes the PB pretreatment temperature (423, 523, or 573 K). (a–e) Temperature dependence of electrical conductivity σ , Seebeck coefficient S , power factor PF , weighted mobility μ_w , and zT , respectively. (f) Pisarenko plot of S versus hole concentration p_h , together with SPB calculations for scattering parameters $r = -0.5$ and -0.25 . (g) Total thermal conductivity κ_{tot} and estimated lattice thermal conductivity κ_{lat} as functions of temperature. (h) Experimental κ_{lat} values of pristine BST and the transport-optimized BST/0.8 wt% 573 K PB composite, together with Debye–Callaway-model fits incorporating different phonon-scattering terms [35]. (i) Schematic cumulative κ_{lat} as a function of phonon frequency, illustrating the contributions of grain-boundary, point-defect, second-phase, and nanopore scattering.

To examine whether the enhanced working-temperature-averaged zT of the PB-modified BST composite can be

translated into practical device performance, we performed numerical geometry optimization and fabricated a prototype thermoelectric generator. A two-pair module was designed using BST/0.8 wt% 573 K PB as the *p*-type leg material and $\text{Mg}_3(\text{Bi,Sb})_2$ as the *n*-type leg material. The maximum conversion efficiency, $\eta_{\max}$, was first calculated as a function of the *p*-to-*n*-type leg cross-sectional-area ratio, A_p/A_n , and the normalized heat-transfer parameter, H/A_{pn} , at $T_c = 300$ K.

As shown in Figure 7c, a broad high-efficiency plateau is centered at $A_p/A_n \approx 1.4 - 1.8$, whereas $\eta_{\max}$ varies comparatively modestly with H/A_{pn} over the investigated range. This result indicates that matching the cross-sectional areas of the *p*- and *n*-type legs is the more influential geometric factor in the present model. The calculated efficiency reaches approximately 8.5% within the optimized region, and the dimensions of the experimental module were selected accordingly. This calculated value represents an idealized device-level prediction and should not be directly equated with the experimentally measured efficiency, because practical modules additionally contain electrical and thermal contact resistances and other parasitic heat losses.

The fabricated two-pair module was subsequently evaluated under temperature differences of $\Delta T = 122, 167, 200$, and 231 K, with the cold-side temperature fixed at $T_c = 300$ K. Figure 7a shows the measured U - I and P - I characteristics. Increasing ΔT produces systematic increases in both the open-circuit voltage and the maximum output power, as expected from the increased thermoelectric driving force.

The corresponding efficiency-current curves are presented in Figure 7b. At each temperature difference, the efficiency initially increases with current, reaches a maximum at an intermediate operating current, and subsequently decreases because of load mismatch and increased Joule-heating losses.

At the highest tested temperature difference of $\Delta T = 231$ K, corresponding to $T_h \approx 531$ K and $T_c = 300$ K, the module achieves a maximum measured conversion efficiency of approximately 7.0%. The difference between the idealized calculated efficiency and the experimentally measured value can be attributed, at least in part, to contact resistance, interfacial thermal resistance, and parasitic heat leakage in the practical device.

The measured $\eta_{\max}$ values are compared in Figure 7d with those of representative low-temperature thermoelectric modules reported previously [36–39]. The BST/0.8 wt% 573 K PB-based module exhibits competitive conversion performance within the investigated temperature span. Nevertheless, this comparison is intended primarily to establish the device-level performance range of the present prototype, because differences in thermoelectric-leg compositions, module geometry, contact resistance, heat-input determination, and test configuration prevent a strict one-to-one comparison among the reported modules. The underlying benchmark data are summarized in Table S5 in the ESM.

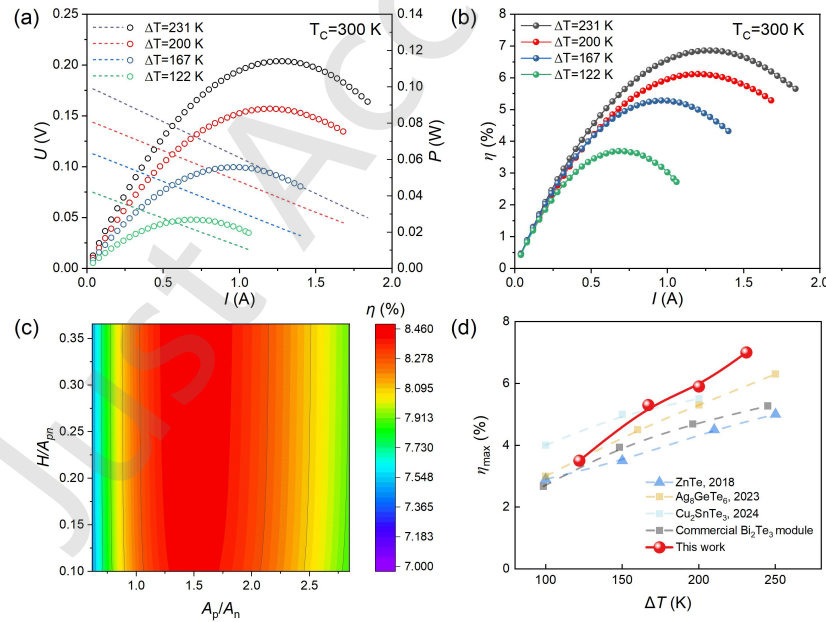


Figure 7. Device-level performance of a two-pair thermoelectric module using transport-optimized BST/0.8 wt% 573 K PB as the *p*-type leg material and $\text{Mg}_3(\text{Bi,Sb})_2$ as the *n*-type leg material, with the cold-side temperature fixed at 300 K. (a) Measured voltage–current (U - I , dashed lines, left axis) and power–current (P - I , open symbols, right axis) characteristics at $\Delta T = 122, 167, 200$, and 231 K. (b) Measured conversion efficiency, η , as a function of current at the same temperature differences. (c) Calculated maximum conversion efficiency, $\eta_{\max}$, as a function of the *p*- to *n*-type leg cross-sectional-area ratio, A_p/A_n , and the normalized heat-transfer parameter, H/A_{pn} , at $T_c = 300$ K. (d) Comparison of the maximum measured conversion efficiency of this work with representative low-temperature thermoelectric modules as a function of ΔT [36–39].

Conclusion

Prussian-blue-derived frameworks were introduced as structurally tunable second phases in $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$. Thermal pretreatment transforms crystalline PB into an amorphous framework that loses long-range periodicity while retaining short-range Fe–C–N coordination, mixed Fe valence, and mesoporous features. Microscopic and spectroscopic characterization of the PB-modified BST composites further supports the presence of PB-derived interfacial domains and establishes the structural basis for their influence on thermoelectric transport.

Compared with crystalline PB, the amorphous PB-derived framework more effectively suppresses lattice thermal conductivity through enhanced structural disorder, heterogeneous interfaces, reduced phonon group velocities, and pore-related phonon scattering, while only moderately compromising electronic transport. The optimized BST/0.8 wt% 573 K PB composite reaches a peak zT of approximately 1.56 and an average zT of approximately 1.27 over 300–500 K. A two-pair prototype module delivers a measured conversion efficiency of about 7.0% at $\Delta T = 231$ K, demonstrating that the improved material-level performance can be translated into device-level performance. Overall, the zT enhancement is governed primarily by the pronounced suppression of κ_{lat} , while Seebeck enhancement and moderately preserved electrical transport help maintain a favorable power-factor/thermal-conductivity balance, rather than producing an improvement through power-factor maximization alone.

Electronic Supplementary Material: Supplementary material is available in the online version of this article. It includes additional SAED/bright-field TEM images of PB amorphization (Fig. S1), representative SEM and TEM images (Fig. S2–S4), Raman and thermogravimetric data (Figs. S5 and S6), charge-density-difference calculations (Fig. S7), Bi/Sb/Te edge XAFS data (Fig. S8), full loading-dependent transport results (Fig. S9), repeatability and cyclic stability data for the optimized sample (Figs. S10 and S11), and supporting density, fitting, average- zT , and benchmark tables (Tables S1–S5).

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors declare no conflict of interest.

Author contribution statement

Tianyi Ma conceived the research, designed and carried out the experiments, performed data analysis, and wrote the original draft of the manuscript. Pengfei Xu and Gen Zhang contributed to conceptualization, provided critical guidance on data interpretation, and revised the manuscript. Hao Yang and Yezhen Hua assisted with sample preparation, characterization, and data analysis. Biao Xu supervised the project, secured funding, guided the research direction, and critically revised the manuscript. All authors discussed the results and approved the final version of the manuscript.

Use of AI statement

None.

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Amorphous framework doping of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ thermoelectrics via Prussian Blue-derived phases

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Supplementary Contents

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Section S2. Calculation details

Section S3. Single-parabolic-band (SPB) analysis and weighted mobility

Section S4. Debye–Callaway analysis of lattice thermal conductivity

Section S5. Additional device fabrication and measurement details

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Section S7. References

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Section S1. Experimental details and characterizations

Chemicals and materials

Commercial crystalline Prussian blue (PB; Aladdin, AR) was used as the precursor framework phase as received without further purification. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, AR, Nanjing Reagent), bismuth chloride (BiCl_3 , AR, Aladdin), antimony trichloride (SbCl_3 , AR, Aladdin), tellurium powder (Te, 99.99%, Macklin), sodium hydroxide (NaOH, 98%, Alfa Aesar), and sodium borohydride (NaBH_4 , AR, SCRC) were used for the hydrothermal synthesis of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ (BST). Deionized water and absolute ethanol were used during the synthesis, washing, and dispersion steps. Unless otherwise specified, all chemicals and reagents were used as received without further purification.

Sample nomenclature. In this work, BST denotes $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, and PB denotes the untreated crystalline Prussian blue precursor. Experimentally heat-treated samples are uniformly denoted x K PB, where x represents the PB pretreatment temperature before composite preparation. This processing-based designation identifies the pretreatment condition and does not imply that the treated sample remains crystalline. The actual structural state of each sample is determined from the corresponding structural and spectroscopic characterization. PB-g denotes the amorphous or glassy PB-derived framework that lacks long-range order while retaining local Fe–C–N coordination. It is used as a structural descriptor and for the periodic disordered-supercell model in the computational discussion, rather than as the name of a specific experimental sample. Composite samples are written as BST/ y wt% x K PB, where y is the PB-derived-phase loading. The 10 wt% composites are structural/spectroscopic model samples used to enhance weak framework-related signals, whereas BST/0.8 wt% 573 K PB is the transport-optimized composite and the p-type leg material used in the thermoelectric module.

Preparation of PB-derived framework phases

Commercial crystalline PB powder was used as received as the untreated precursor. To tune the structural state of the framework, PB was thermally pretreated at selected temperatures between 423 and 573 K, yielding a series of experimental samples denoted x K PB, where x is the pretreatment temperature before composite preparation. This notation specifies the processing condition only; the crystalline, partially amorphized, or strongly amorphized state of each sample is assigned from the corresponding structural and spectroscopic results. Accordingly, the untreated precursor is denoted PB, whereas the heat-treated samples are denoted 423 K PB, 473 K PB, 523 K PB, 543 K PB, 558 K PB and 573 K PB as applicable. PB-g is used only as a structural descriptor for the amorphous or glassy PB-derived framework and as the name of the periodic disordered-supercell model, not as an experimental sample designation.

Preparation of BST and PB-modified BST composites

BST powder with the nominal composition $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ was synthesized by a hydrothermal method. EDTA-2Na (0.6 g), BiCl_3 (0.7568 g), SbCl_3 (2.19 g), Te powder (2.772 g), and NaOH (5 g) were added to 120 mL of deionized water in a Teflon-lined autoclave and vigorously stirred to obtain a homogeneous mixture. NaBH_4 (2 g) was then added as the reducing agent. The autoclave was sealed and heated at 200 °C for 12 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed twice with deionized water and twice with absolute ethanol, and vacuum-dried at 60 °C for 12 h.

For the preparation of BST/ y wt% x K PB composites, the selected PB or x K PB powder was first ultrasonically dispersed in ethanol. The as-prepared BST powder was then added to the suspension and further ultrasonically dispersed to promote homogeneous mixing. The mixed suspension was magnetically stirred at room temperature for 1 h and vacuum-dried at 40 °C for 12 h. The dried composite powders were subsequently subjected to spark plasma sintering. Here, y denotes the PB-derived-phase loading and x denotes the PB pretreatment temperature; composites containing untreated PB are identified explicitly as pristine-PB model composites where needed.

Spark plasma sintering (SPS)

The dried BST powder and BST/ y wt% x K PB composite powders were lightly ground to break up soft agglomerates and then loaded into a graphite die with an inner diameter of approximately 10 mm. The powders were consolidated under vacuum by spark plasma sintering using a LABOX-110 system. The sintering temperature was maintained at approximately 543 K under an applied pressure of 60 MPa, with a holding time of 5 min.

A two-step low-temperature SPS procedure was employed. After the first short-duration pressure-assisted consolidation, the resulting compacts were removed from the graphite die, gently crushed, and reground to improve the dispersion uniformity of the PB-derived second phase within the BST matrix. The powders were then subjected to a second SPS consolidation under the same low-temperature conditions. This two-step procedure was designed to promote densification and improve the distribution of PB-derived species while minimizing excessive thermal degradation of the cyanide-coordinated framework.

The relatively mild sintering temperature and short holding time help limit extensive decomposition of the cyanide-coordinated PB framework. After consolidation, the PB-derived species are expected to be distributed mainly near BST grain-boundary regions, forming a heterogeneous interfacial network containing disordered PB-derived domains and multiscale interfaces.

Specimen preparation for thermoelectric measurements

For each composition, the electrical-transport bar and thermal-diffusivity disk were cut from the same SPS-consolidated

cylindrical pellet after the graphite-contacted surface layer had been removed by grinding and polishing. Electrical specimens were cut with the long axis perpendicular to the SPS pressing direction and polished to approximately 3 mm × 3 mm × 10 mm. Thermal-diffusivity specimens were machined into disks of approximately 10 mm × 10 mm × 1 mm, so that the through-thickness heat-flow direction was also perpendicular to the SPS pressing direction; the specimens were measured using a DXF-900 flash-diffusivity instrument. Therefore, the electrical-transport and thermal-diffusivity data used for zT determination were obtained along the same direction. Thermal conductivity was calculated from $\kappa = DC_p\rho$. C_p was estimated using the Dulong–Petit approximation, and ρ was determined from the mass and geometric volume of the same disk specimens. The corresponding density and relative-density values are summarized in Table S1.

Table S1. Bulk density and relative density of SPS-consolidated pristine BST and PB-modified BST composites.

Sample	Density (g cm ⁻³)	Relative density (%)
BST	6.62	97.6
BST/0.2 wt% 573 K PB	6.61	97.5
BST/0.5 wt% 573 K PB	6.60	97.3
BST/0.8 wt% 573 K PB	6.59	97.0
BST/1.0 wt% 573 K PB	6.57	96.5
BST/0.8 wt% 423 K PB	6.53	96.3
BST/0.8 wt% 523 K PB	6.56	96.7

Structural and chemical characterizations

Powder X-ray diffraction (PXRD). The PXRD patterns of the as-prepared samples were collected on a Bruker D8 Advance powder diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$; 40 kV; 40 mA). The data were recorded with a step size of 0.02° under ambient atmosphere at room temperature.

Scanning electron microscopy (SEM). The fractured surfaces of the sintered samples were characterized by scanning electron microscopy (SEM, JSM-IT500HR, JEOL).

Transmission electron microscopy (TEM). Low-magnification TEM images and high-resolution TEM images were obtained on an FEI Titan 80-300 microscope operated at 300 kV.

Thermogravimetric analysis (TGA). TGA measurements were carried out on a thermal gravimetric analyzer (TGA 5500).

Fourier transform infrared spectroscopy (FT-IR). FT-IR spectra of the as-prepared samples were recorded on a Thermo Nicolet iS50 spectrometer in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Raman spectroscopy. Raman spectra were obtained using a Thermo Fischer DXR Raman microscope with a 532 nm laser.

N₂ adsorption–desorption analysis. N₂ adsorption–desorption measurements were conducted on a Micromeritics ASAP 2460 Surface Area and Porosimetry Analyzer at 77 K using ultra-high-purity N₂. All samples were degassed at 120 °C for 10 h before the measurements.

Pair distribution function (PDF). The pair distribution function data reduction, background subtraction, and absorption correction were carried out using PDFgetX, and the structural refinements were performed using PDFgui.

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed on a PHI5000 Versa Probe system (ULVAC-PHI, Japan) using monochromatic Al K α radiation as the X-ray source.

X-ray absorption fine structure (XAFS). Hard XAFS spectra were collected at the Shanghai Synchrotron Radiation Facility (SSRF) and the HXMA beamline of the Canadian Light Source (CLS) under air atmosphere at room temperature using transmission and fluorescence modes. The powder samples were pressed into 13 mm wafers according to the element content. The XAFS data were processed using Athena and Artemis software.

Thermoelectric transport and Hall measurements. The electrical conductivity σ and Seebeck coefficient S were measured simultaneously using the static direct-current and four-probe methods (CTA-3S, CRYALL), with an estimated uncertainty of approximately 5% for each. Thermal diffusivity D was measured on the disk specimen using a DXF-900 flash-diffusivity instrument along the direction perpendicular to the SPS pressing direction. Thermal conductivity was calculated as $\kappa = DC_p\rho$, where C_p was estimated using the Dulong–Petit approximation and ρ was determined from the mass and geometric volume of the same disk specimen. The uncertainty of κ was estimated to be within 10%, and the combined uncertainty in zT was below 20%. The charge carrier concentration p_H and Hall mobility μ_H were determined from the Hall coefficient R_H measured under a reversible magnetic field of 1.5 T using the van der Pauw method (Lake Shore 8400 Series, Model 8404, USA), according to $p_H = 1/(eR_H)$ and $\mu_H = \sigma R_H$, respectively.

Section S2. Calculation details

All first-principles calculations were carried out within the framework of density functional theory (DFT). The projector-augmented wave (PAW) method was employed to describe the core–valence interaction[1,2] and the exchange–correlation energy was treated using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).[3] A plane-wave kinetic-energy cutoff of 500 eV was used for the electronic-structure calculations, and the Brillouin zone was sampled using a Γ -centered k-point scheme. Structural relaxation was performed until the total-energy convergence threshold was better than 10⁻⁶ eV and the residual Hellmann–Feynman force on each atom was below 0.03 eV $\text{\AA}^{-1}$.

For crystalline PB, the initial structure was built from the experimentally reported Prussian blue framework and subsequently optimized before the electronic and vibrational calculations. For the BST matrix, the Bi_{0.4}Sb_{1.6}Te₃ structure was constructed on the basis of the reported rhombohedral Bi_{0.4}Sb_{1.6}Te₃ crystal structure and treated using a representative ordered-supercell substitution approximation. For the amorphous/glassy framework PB-g, the structural model was generated from the

crystalline PB framework by introducing local structural distortions and symmetry breaking, followed by full structural relaxation to obtain a disordered supercell that preserves the short-range Fe–C–N coordination while lacking long-range periodicity. The computational models were chosen to reproduce the qualitative differences between crystalline PB and PB-g rather than to represent a unique atomically resolved interface structure.

Electronic band structures

The electronic band structures of PB and PB-g were calculated on the optimized structures using the converged self-consistent charge density. As shown in the main text, both PB and PB-g are wide-band-gap insulating framework phases, with calculated band gaps of approximately 2.1 eV and 1.5 eV, respectively. In both cases, the bands near the Fermi level are relatively flat, indicating strong electronic localization and intrinsically low carrier mobility. These results support the interpretation that PB-derived framework domains do not act as extended conductive phases after incorporation into the $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ matrix, and that their electronic influence is more plausibly exerted through localized interfacial effects such as charge redistribution and carrier modulation.

Phonon calculations

The phonon dispersion relations, phonon density of states (PDOS), and phonon group velocities were calculated using the Phonopy package on the basis of the DFT-relaxed structures.[4] The calculations were designed to compare the vibrational characteristics of crystalline PB, glassy PB-g, and the BST matrix.

The calculated phonon dispersions show that most vibrational branches of PB are located below approximately 15 THz, together with a set of nearly flat optical modes arising from localized framework vibrations. An additional isolated high-frequency branch appears around 60–70 THz and is attributed to the $\text{C}\equiv\text{N}$ stretching vibrations. After amorphization, the phonon spectrum of PB-g becomes more congested and less dispersive, indicating enhanced vibrational disorder and localization in the glassy network. The calculated phonon group velocities further show that PB-g exhibits systematically lower group velocities than crystalline PB in the low-frequency region most relevant to heat transport.

Phonon density of states (PDOS)

The total phonon density of states was calculated for PB, PB-g, and $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ in order to compare their vibrational spectra. PB and PB-g both possess a broad low-frequency phonon band below ~20 THz that partially overlaps with the phonon spectrum of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, enabling vibrational coupling at the interface. At the same time, the broader spectral differences and the enhanced disorder of the amorphous framework are expected to promote interfacial phonon scattering in the composite. By contrast, the high-frequency $\text{C}\equiv\text{N}$ stretching modes lie far above the cutoff frequency of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ and therefore contribute little to the heat transport of the thermoelectric matrix.

Remarks on model interpretation

The present calculations were intended to clarify the intrinsic vibrational and electronic characteristics of the PB-derived framework phases rather than to provide an atomically unique model of every possible BST/PB interface. Accordingly, the calculated band structures and phonon spectra were mainly used to rationalize three experimentally observed trends in the main text: (i) PB-derived domains do not form an extended conductive phase in the BST matrix, (ii) the amorphous framework shows stronger phonon-glass-like behavior than crystalline PB, and (iii) the partial low-frequency vibrational overlap between PB-derived frameworks and BST allows interfacial coupling while structural disorder and spectral mismatch enhance phonon scattering.

Section S3. Single-parabolic-band (SPB) analysis and weighted mobility

To evaluate the electronic transport behavior of the PB-modified BST composites, the experimental Seebeck coefficient, Lorenz number, and weighted mobility were analyzed within a single-parabolic-band (SPB) framework under the assumption that charge-carrier scattering is dominated by acoustic phonons.

Within this model, the Lorenz number L is given by

$$L = \left(\frac{k_B}{e}\right)^2 \frac{3F_0(\eta)F_2(\eta) - 4F_1(\eta)^2}{F_0(\eta)^2} \quad (\text{S1})$$

where k_B is the Boltzmann constant, e is the elementary charge, and η is the reduced Fermi level. The reduced Fermi level can be obtained from the measured Seebeck coefficient through

$$S = -\left(\frac{k_B}{e}\right) \left[\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right] \quad (\text{S2})$$

The Fermi integral $F_n(\eta)$ is defined as

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + \exp(\chi - \eta)} d\chi \quad (\text{S3})$$

Using the reduced Fermi level derived from the Seebeck coefficient, the density-of-states effective mass m_{DOS}^* can be estimated as

$$m_{\text{DOS}}^* = \frac{h^2}{2k_B T} \cdot \left[\frac{n r_H}{4\pi F_{1/2}(\eta)} \right]^{2/3} \quad (\text{S4})$$

where h is Planck's constant, T is the absolute temperature, n is the carrier concentration, and r_H is the Hall factor from the standard SPB treatment for acoustic-phonon scattering.

The weighted mobility shown in Figure 6d of the main text was calculated from the measured electrical resistivity and Seebeck coefficient according to

$$\mu_w = 331 \left(\frac{1}{\rho} \right) \left(\frac{T}{300} \right)^{-3/2} \frac{\exp \left[\left(\frac{|S|}{k_B/e} \right) - 2 \right]}{1 + \exp \left[5 \left(\left(\frac{|S|}{k_B/e} \right) - 1 \right) \right]} \quad (\text{S5})$$

where μ_w is expressed in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, ρ is the electrical resistivity in $\text{m}\Omega \text{cm}$, T is in K, and $k_B/e = 86.3 \mu\text{V K}^{-1}$. In the present work, the SPB model was employed as a convenient baseline for correlating the measured Seebeck coefficient, Lorenz number, carrier concentration, and weighted mobility. Comparison between the experimental data and the SPB-derived trends helps identify whether the transport evolution after PB incorporation can be explained solely by carrier-density variation or whether additional transport modulation is involved.

Section S4. Debye–Callaway analysis of lattice thermal conductivity

Within the Debye–Callaway formalism, the lattice thermal conductivity κ_{lat} is calculated by assuming that heat is mainly carried by acoustic phonons, and is expressed as

$$\kappa_{\text{lat}} = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau_{\text{tot}}(x) \cdot \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{S6})$$

where k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant, $x = \hbar\omega/k_B T$, ω is the phonon angular frequency, v is the average sound velocity, θ_D is the Debye temperature, and τ_{tot} is the total phonon relaxation time. According to Matthiessen's rule, the total phonon scattering rate is written as

$$\tau_{\text{tot}}^{-1} = \tau_U^{-1} + \tau_N^{-1} + \tau_{GB}^{-1} + \tau_{PD}^{-1} + \tau_{SP}^{-1} + \tau_{NP}^{-1} \quad (\text{S7})$$

where the subscripts U , N , GB , PD , SP , and NP denote Umklapp phonon–phonon scattering, normal phonon–phonon scattering, grain-boundary scattering, point-defect scattering, second-phase scattering, and nanopore scattering, respectively.

The combined contribution of Umklapp and normal phonon–phonon scattering was treated using an effective expression: [5,6]

$$\tau_U^{-1} + \tau_N^{-1} = A \cdot \frac{2k_B \cdot V^{1/3} \cdot \gamma \cdot \omega \cdot 2 \cdot T}{(6\pi^2)^{1/3} \cdot M \cdot v^3} \quad (\text{S8})$$

where A is an effective fitting coefficient, $\bar{V}$ is the average atomic volume, γ is the Grüneisen parameter, T is the absolute temperature, and $\bar{M}$ is the average atomic mass.

The grain-boundary scattering rate is expressed as

$$\tau_{GB}^{-1} = \frac{v}{d} \quad (\text{S9})$$

where d is the average grain size.

The point-defect scattering rate is written as: [8]

$$\tau_{PD}^{-1} = \frac{\bar{V} \omega^4 \Gamma}{4\pi v^3} \quad (\text{S10})$$

where Γ is an effective point-defect scattering parameter. For the PB-derived composite, additional second-phase and nanopore terms were included to account for the stronger suppression of κ_{lat} .

When the PB-derived domains and nanopores are approximated as spherical scattering centers, their contribution can be written as: [8–10]

$$\tau_i^{-1} = v \left(\sigma_{s,i}^{-1} + \sigma_{l,i}^{-1} \right) V_i \quad (\text{S11})$$

$$\sigma_{s,i} = 2\pi R_i^2 \quad (\text{S12})$$

$$\sigma_{l,i} = \frac{4}{9} \pi R_i^2 \left(\frac{\Delta\rho_i}{\rho_m} \right)^2 \left(\frac{R_i \omega}{v} \right)^4 \quad (\text{S13})$$

Here i represents either PB-derived second phases (SP) or nanopores (NP), R_i is the characteristic radius of the corresponding scattering center, V_i is its number density, ρ_m is the matrix density, and $\Delta\rho_i$ is the density contrast between the matrix and the scattering center. In the fitting procedure, A and Γ were treated as effective fitting coefficients for the intrinsic channels, whereas the composite-specific parameters were introduced only for BST/0.8 wt% 573 K PB.

Table S2. Parameters used in the Debye–Callaway analysis for pristine BST.

Parameter	Notes	Values	Methods
v	Average speed of sound	1749 m s^{-1}	Assumed / fitted initial value
v_L	Longitudinal speed of sound	3120 m s^{-1}	Assumed
v_T	Transverse speed of sound	1560 m s^{-1}	Assumed
θ_D	Debye temperature	166 K	Calculated from v and $\bar{V}$
$\bar{V}$	Average atomic volume of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	$3.10 \times 10^{-29} \text{ m}^3$	Estimated
$\bar{M}$	Average atomic mass of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	$2.20 \times 10^{-25} \text{ kg}$	Calculated from composition
γ	Grüneisen parameter	1.4	Assumed
d	Effective grain size	500 nm	Assumed from polycrystalline BST

Table S3. Effective parameters used in the Debye–Callaway analysis for BST/0.8 wt% 573 K PB.

Parameter	Notes	Values	Methods
v	Average speed of sound	1749 m s ⁻¹	Same as BST host
v_L	Longitudinal speed of sound	3120 m s ⁻¹	Same as BST host
v_T	Transverse speed of sound	1560 m s ⁻¹	Same as BST host
θ_D	Debye temperature	166 K	Same as BST host
V	Average atomic volume of Bi _{0.4} Sb _{1.6} Te ₃	3.10×10^{-29} m ³	Same as BST host
M	Average atomic mass of Bi _{0.4} Sb _{1.6} Te ₃	2.20×10^{-25} kg	Same as BST host
γ	Grüneisen parameter	1.4	Same as BST host
d	Effective grain size in composite	300 nm	Assumed / effective
d_{NP}	Characteristic nanopore size	30–80 nm	Estimated from pore-size analysis
d_{SP}	Characteristic second-phase/domain size	50–150 nm	Estimated from TEM/EDS
A_{SP}	Second-phase scattering strength	Fitting parameter	Fitted
A_{NP}	Nanopore scattering strength	Fitting parameter	Fitted

Section S5. Additional device fabrication and measurement details

To evaluate whether the improved average thermoelectric performance of the PB-modified BST composites can be translated into practical device output, a 2-pair thermoelectric module was fabricated using BST/0.8 wt% 573 K PB as the p-type leg material and Mg₃(Bi,Sb)₂ as the n-type leg material. The device geometry was selected according to the numerical optimization presented in the main text, where the maximum conversion efficiency $\eta_{\max}$ was calculated as a function of the cross-sectional area ratio of the p- and n-type legs (A_p/A_n) and the normalized heat-transfer parameter H/A_{pn} at $T_c = 300$ K. The final leg dimensions used for the prototype module were chosen within the broad optimized region of the $\eta_{\max}$ map.

For module-performance measurements, the hot side of the device was brought into contact with a controllable heater, while the cold side was maintained at 300 K using a water-cooled heat sink. High-temperature thermal grease was applied at the interfaces to reduce interfacial thermal resistance. The output voltage U and current I were recorded by varying the external load resistance, and the output power was calculated using $P = UI$. The current–voltage and current–power characteristics were measured under several temperature differences, namely $\Delta T = 122, 167, 200$, and 231 K, with T_c fixed at 300 K, consistent with the measurements shown in the main text.

The conversion efficiency η was evaluated under steady-state conditions from the ratio of electrical output power to heat input according to $\eta = P/Q_{in}$, where P is the electrical output power and Q_{in} is the heat-input rate into the device. For each measurement point, the external load was adjusted until stable output voltage and current values were obtained. The corresponding η – I curves were then derived from the measured electrical output and heat-input data.

At the highest tested temperature difference of $\Delta T = 231$ K ($T_h \approx 531$ K, $T_c = 300$ K), the BST/0.8 wt% 573 K PB-based module reaches a maximum conversion efficiency of approximately 7.0%, which is higher than that of the undoped BST reference module measured under similar conditions. The benchmark dataset used for comparison with representative low-temperature modules is summarized in Table S5.

Section S6. Supplementary Figures and Tables

Table S4. Working-temperature-averaged zT values of pristine BST and BST/0.8 wt% x K PB composites over 300–500 K.

Sample	zT_{avg} (300–500 K)
Pristine BST	1.01
BST/0.8 wt% 423 K PB	1.19
BST/0.8 wt% 523 K PB	1.10
BST/0.8 wt% 573 K PB	1.27

Table S5. Benchmark comparison of the maximum conversion efficiency with representative low-temperature thermoelectric modules.

Device / material system	p-type leg	n-type leg	ΔT (K)	$\eta_{\max}$ (%)	Source
This work	BST/0.8 wt% 573 K PB	Mg ₃ (Bi,Sb) ₂	231	7.0	This work
ZnTe-nanostructured Bi _{0.46} Sb _{1.54} Te ₃ module	ZnTe-nanostructured Bi _{0.46} Sb _{1.54} Te ₃	Conventional BiTeSe	250	5.0	Energy Environ. Sci. 2018 [11]
Ag ₈ GeTe ₆ -assisted (Bi,Sb) ₂ Te ₃ module	Bi _{0.4} Sb _{1.6} Te _{2.95} Se _{0.05} + 0.10 wt% Ag ₈ GeTe ₆	Not reported	245	6.3	Adv. Mater. 2023 [12]
Cu ₂ SnTe ₃ -modified Bi _{0.5} Sb _{1.5} Te ₃ module	Cu ₂ SnTe ₃ -modified Bi _{0.5} Sb _{1.5} Te ₃	Zone-melted Bi ₂ Te _{2.7} Se _{0.3}	Not reported	~6.0	J. Mater. Chem. A 2024 [13]
Commercial Bi ₂ Te ₃ module	Commercial Bi ₂ Te ₃ -based	Commercial Bi ₂ Te ₃ -based	250	7.2	Measurement 2021 [14]

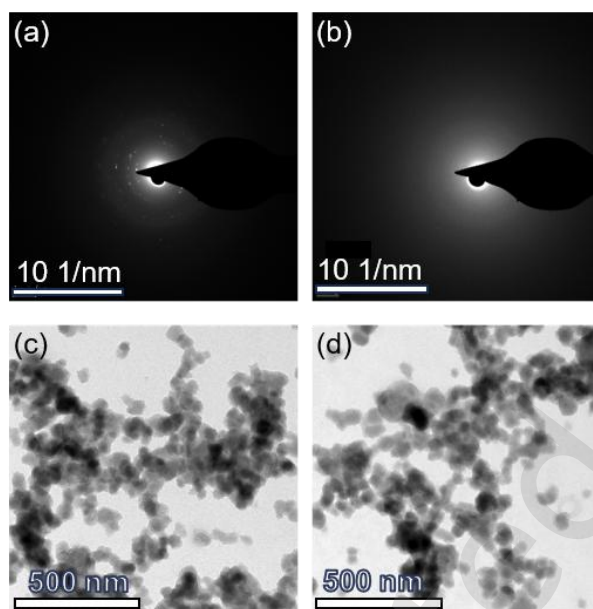


Figure S1. Selected-area electron diffraction (SAED) patterns and bright-field TEM images of Prussian blue (PB) before and after thermal treatment. (a, c) Pristine PB; (b, d) 573 K PB (strongly amorphized PB-derived state). The pristine sample exhibits distinct diffraction spots, indicative of long-range crystallinity, whereas the heat-treated sample shows a diffuse halo, confirming the loss of long-range order. The TEM images indicate that the aggregated nanoparticle morphology is largely retained after thermal treatment.

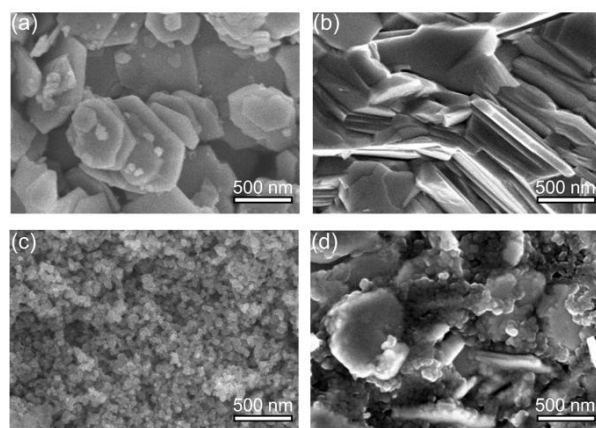


Figure S2. SEM images of representative starting materials and SPS-consolidated samples used in this work. (a) Pristine $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ (BST) powder, (b) pristine BST after SPS consolidation, (c) pristine crystalline PB powder, and (d) the BST/10 wt% pristine PB structural/spectroscopic model composite after SPS consolidation. The images provide morphological context for the starting powders and consolidated materials. The high-loading composite is shown to enhance the visibility of PB-related particulate features and is not treated as a direct microstructural substitute for the transport-optimized BST/0.8 wt% 573 K PB composite.

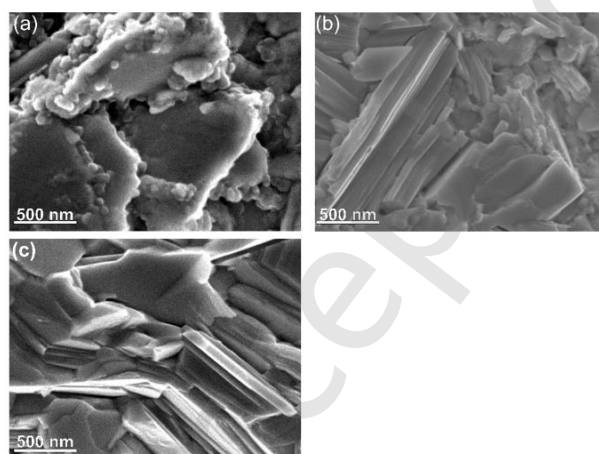


Figure S3. SEM images of the fractured surfaces of SPS-consolidated BST and PB-modified BST composites. (a) BST/10 wt% 573 K PB structural/spectroscopic model composite, showing abundant nanoscale particulate features on or near the BST grains. (b) Transport-optimized BST/0.8 wt% 573 K PB composite, showing retained plate-like BST morphology, substantially fewer nanoscale particulate features, and no obvious large-scale aggregation. (c) Pristine BST without PB addition, showing relatively clean plate-like grains and no obvious nanoscale particulate decoration. The decrease in particulate-feature density with decreasing PB loading supports an association with the PB-derived phase. Because SEM contrast alone cannot establish chemical identity, these features are described morphologically and are interpreted together with the TEM and compositional evidence.

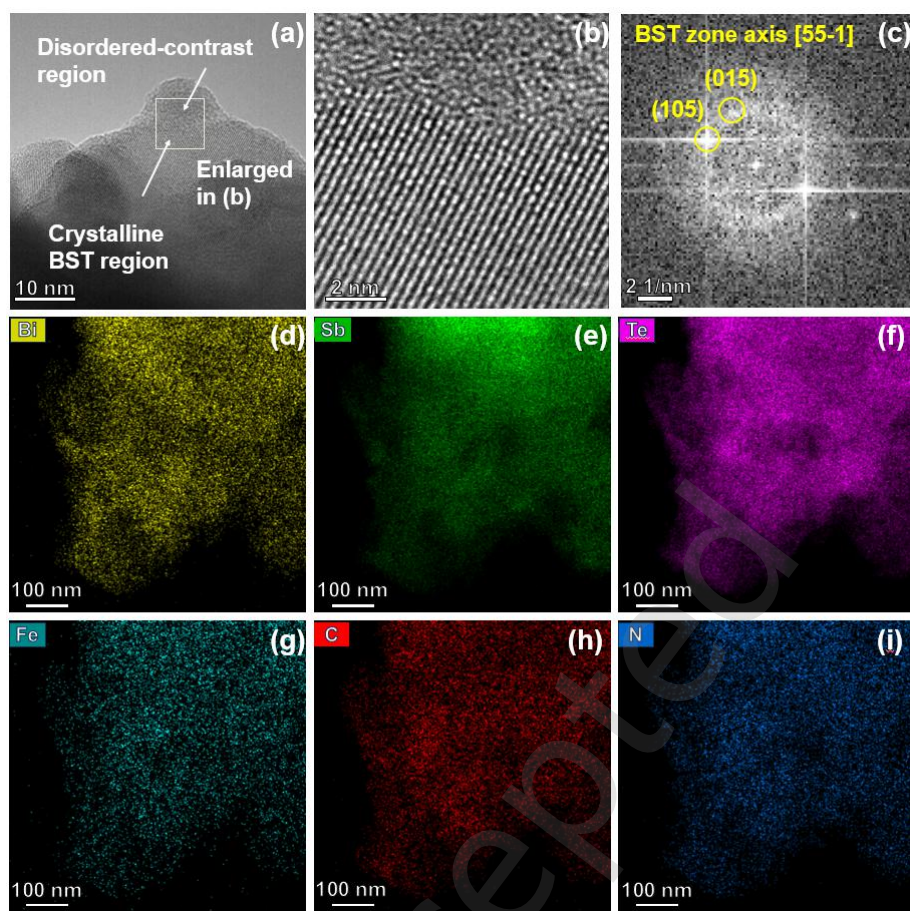


Figure S4. Microscopic characterization of the transport-optimized BST/0.8 wt% 573 K PB composite after SPS. (a) TEM image showing a crystalline BST region adjacent to a region with disordered contrast. The boxed area is enlarged in (b). (b) HRTEM image of the crystalline BST region showing clear lattice fringes. (c) FFT pattern obtained from the lattice-fringe region in (b), tentatively indexed to the $[55\bar{1}]$ zone axis of BST. (d–i) STEM-EDS maps of Bi, Sb, Te, Fe, C, and N acquired from a separate representative region of the same specimen. Bi, Sb, and Te identify the continuous BST matrix, whereas the weaker Fe signal, together with auxiliary C and N signals, supports the presence of finely dispersed PB-derived species. Because the HRTEM and STEM-EDS data were acquired from different representative regions, no one-to-one spatial correlation is claimed.

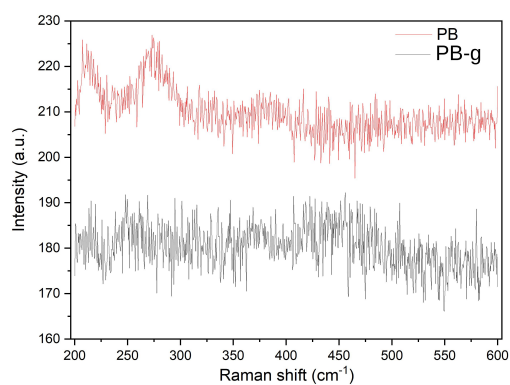


Figure S5. Room-temperature Raman spectra of crystalline PB and 573 K amorphous/glassy PB-g in the 200–600 cm⁻¹ region, showing the broadening and intensity changes of framework-related modes after amorphization.

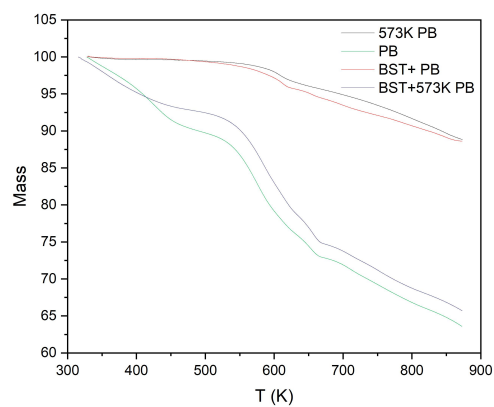


Figure S6. Thermogravimetric curves of PB, PB-derived samples and BST-containing composites measured on heating, showing their mass loss behavior and thermal stability up to about 900 K.

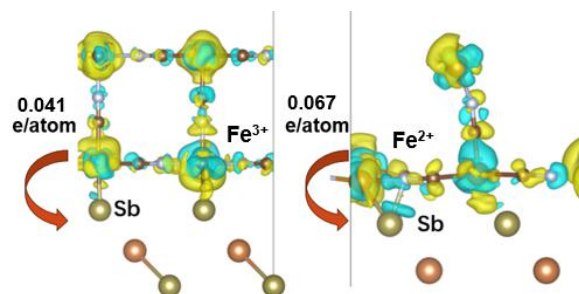


Figure S7. Charge-density-difference isosurfaces for representative PB/BST interface models containing Fe^{3+} -centered (left) and Fe^{2+} -centered (right) local environments. Yellow and cyan regions denote charge accumulation and depletion, respectively. The calculated interfacial charge-transfer magnitudes are approximately 0.041 and 0.067 $e \text{ atom}^{-1}$ for the Fe^{3+} - and Fe^{2+} -containing models, respectively. The results are used qualitatively to compare local interfacial charge redistribution and do not represent a unique atomically resolved interface structure in the experimental composite.

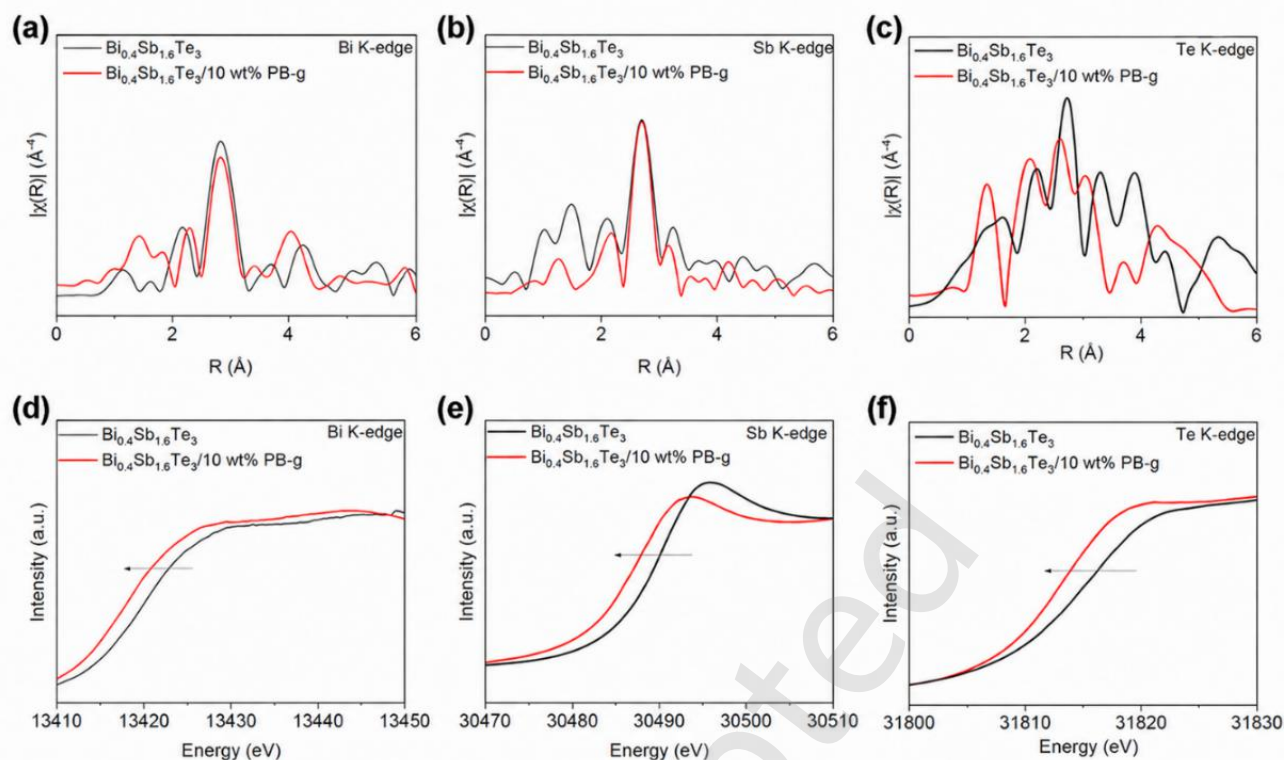


Figure S8. Bi K-edge, Sb K-edge, and Te K-edge Fourier-transformed EXAFS spectra (top row) and normalized XANES spectra (bottom row) of pristine BST and the BST/10 wt% 573 K PB structural/spectroscopic model composite. The principal local coordination features of the BST matrix are retained after incorporation of the PB-derived phase, whereas subtle changes in the EXAFS peak intensity and line shape and in the XANES absorption-edge profiles are consistent with local coordination distortion and interfacial electronic perturbation. The 10 wt% loading was used to enhance the weak framework-related spectral response and does not represent the transport-optimized loading. The panel label “PB-g” is a legacy graphic label for the BST/10 wt% 573 K PB model composite; the experimental sample is referred to as BST/10 wt% 573 K PB throughout the text.

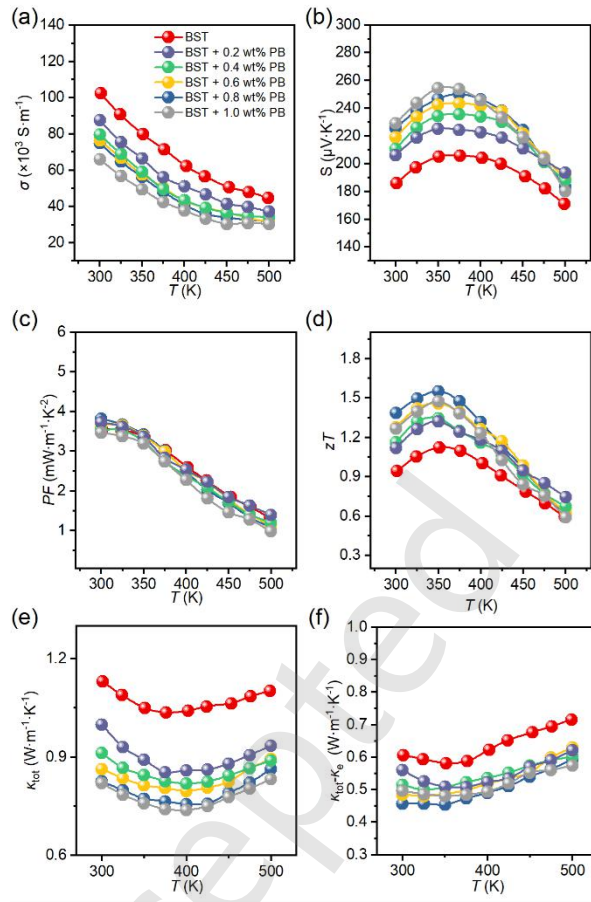


Figure S9. Temperature-dependent thermoelectric transport properties of BST/y wt% 573 K PB composites with different PB-derived-phase loadings: (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) zT , (e) total thermal conductivity, and (f) $\kappa_{\text{tot}} - \kappa_e$. Among the investigated samples, 0.8 wt% 573 K PB shows the highest peak zT , indicating the best balance between electrical transport and thermal-conductivity suppression. The panel legends abbreviate the PB pretreatment condition; all PB-containing samples in this figure were prepared using 573 K PB.

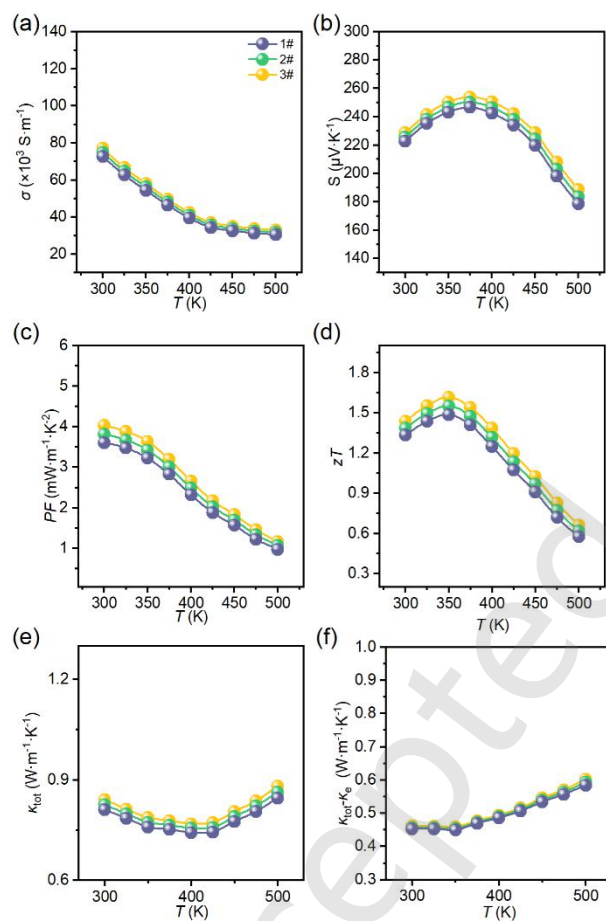


Figure S10. Repeatability of the temperature-dependent thermoelectric properties of the BST/0.8 wt% 573 K PB sample: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF ; (d) figure of merit, zT ; (e) total thermal conductivity, κ_{tot} and (f) $\kappa_{\text{tot}} - \kappa_e$.

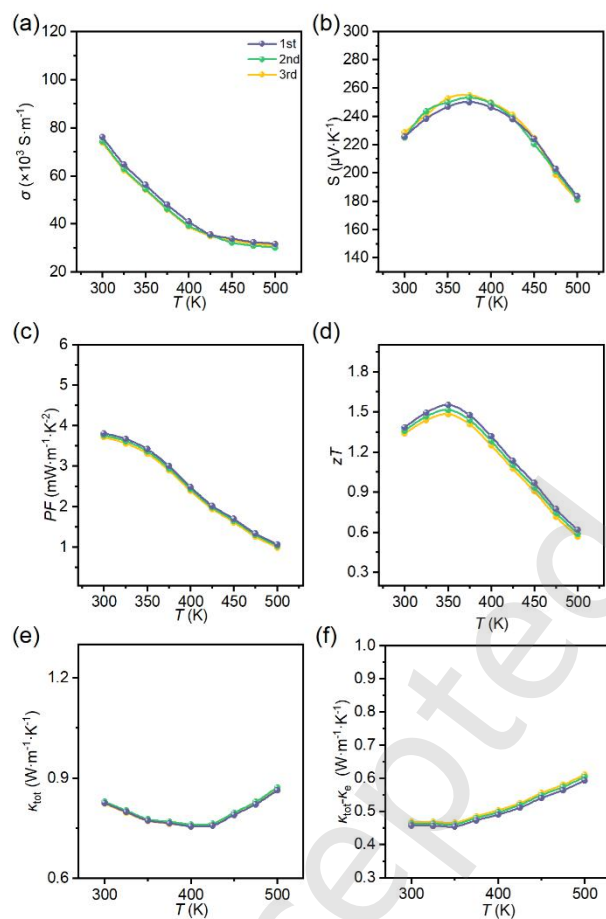


Figure S11. Cyclic stability of the temperature-dependent thermoelectric properties of the BST/0.8 wt% 573 K PB sample over three consecutive measurement cycles: (a) electrical conductivity, σ ; (b) Seebeck coefficient, S ; (c) power factor, PF; (d) figure of merit, zT ; (e) total thermal conductivity, κ_{tot} and (f) $\kappa_{\text{tot}} - \kappa_e$.

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