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Electron microscopy approaches to thermoelectrics: Recent advances and emerging opportunities

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Amid escalating global challenges in energy efficiency and environmental sustainability, the utilization of waste heat has gained significant scientific attention. This growing interest has positioned thermoelectric energy conversion as a pivotal research frontier in materials science, particularly for its potential to transform low-grade thermal energy into usable electricity. Thermoelectric materials hold significant potential in addressing this challenge due to their unique properties, such as the absence of vibration, radiation, and the ability to directly convert heat into electricity. The performance of thermoelectrics is assessed using the dimensionless thermoelectric figure of merit, zT, which is defined as

$$zT = \frac{S^2T}{\rho(\kappa_{\rm E} + \kappa_{\rm L})},$$

where S, σ , T, $\kappa_{\rm E}$, and $\kappa_{\rm L}$ represent the Seebeck coefficient, electrical conductivity, absolute temperature, electronic thermal conductivity, and lattice thermal conductivity, respectively.

The enhancement of thermoelectric efficiency fundamentally relies on the optimization of critical performance parameters, among which κ_L plays a pivotal role. Recent advances in material engineering have demonstrated that strategic approaches including alloying [1], nanostructuring [2], and defect engineering [3] effectively suppress thermal transport by promoting phonon scattering through the introduction of defect structures at multiple length scales. Consequently, a deep understanding of the defect structures and their temporal evolution is essential for optimizing the performance of thermoelectric materials.

Within the spectrum of structural characterization methodologies, electron microscopy has emerged as an indispensable tool for establishing structure-property correlations in thermoelectric materials, primarily due to its unparalleled spatial resolution and comprehensive analytical versatility. Typically, high-resolution transmission electron microscopy (HRTEM) images are employed to identify various defect types, such as dislocations, grain boundaries, phase boundaries, twinning, and precipitates. Comprehensive information including elemental distribution, site occupancy, chemical shifts, electron orbital/spin and bonding, band gap, and valence states can be derived through energy dispersive X-ray spectroscopy and electron energy loss

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spectroscopy (EELS) [4]. Moreover, with the development of aberration-corrected techniques, annular bright field and integrated differential phase contrast technologies facilitate the simultaneous imaging of light and heavy atoms [5], while tomography techniques allow for the three-dimensional visualization of defect structures [6].

The advent of cutting-edge electron microscopy techniques has revolutionized our analytical capabilities, and extended well beyond the aforementioned applications, offering unprecedented opportunities to elucidate fundamental structure-property-performance relationships in thermoelectric systems. In the following sections, we present a comprehensive exploration of promising research directions that leverage these stateof-the-art microscopic approaches. (1) Employing high energy resolution EELS (Figure 1a) [7] to investigate phonon dispersion relationships of defects. This technique aids in understanding thermal conductivity and the interaction between phonons and electrons at the nanoscale, both of which are key factors influencing the efficiency of thermoelectric devices. (2) Easily thermal damaged samples such as fast ion conductors (e.g., Ag₂S [8], Ag₂Se) can be analyzed using cryogenic electron microscopy (cryo-EM) or aberration-corrected electron microscopy equipped with cryo-holders, or using low-dose and four-dimensional scanning transmission electron microscopy (4D-STEM) ptychography (Figure 1b) [9]. It is important to note that prior to utilizing cryogenic technology, it is necessary to employ alternative methods to confirm that the sample will not undergo a phase transition at low temperatures. (3) An *in-situ* chip integrated with micro-electrochemical systems (MEMS) may be capable of measuring the electrical properties of individual thermoelectric materials, including the Seebeck coefficient, electrical conductivity, and power factor (Figure 1c) [10]. The electrical conductivity σ can be calculated by the formula $\sigma = IL/(\Delta VA)$, where L represents the probe spacing, A denotes the cross-sectional area of the sample, I is the current, and ΔV is the potential difference. In contrast, the Seebeck coefficient S is determined by the ratio of voltage (ΔV) to temperature difference (ΔT), expressed as $S = \Delta V / \Delta T$. This approach can facilitate the correlation of thermoelectric properties with the structural and chemical composition of the thermoelectric materials at the atomic level, encompassing grain boundaries, dopants, or crystalline defects, while simultaneously tracking their dynamic evolution during heating or electric current application. (4) The advanced electron microscopy techniques discussed herein can be synergistically integrated to achieve comprehensive material characterization. Notably, the correlative approach combining EELS with ptychography enables simultaneous investigation of phonon dispersion characteristics and defect configurations. Furthermore, the integration of cryo-EM with ptychographic imaging offers a powerful solution for minimizing thermal artifacts while maintaining optimal electron dose conditions for defect structure analysis. Most significantly, the incorporation of *in situ* heating or electrical biasing capabilities with ptychographic techniques facilitates unprecedented opportunities for probing structural evolution under both static and dynamic thermal/electrical stimuli, thereby enabling real-time observation of material responses under operational conditions.

To date, state-of-the-art electron microscopy technologies have emerged as a transformative paradigm in thermoelectric materials research, establishing themselves as indispensable tools for elucidating the complex interplay between diverse defect configurations and their thermoelectric performance. This fundamental understanding at the atomic scale is revolutionizing our approach to materials design, enabling the rational development of next-generation thermoelectric systems with optimized performance characteristics and enhanced operational durability. Notably, these new techniques are currently at an idealized stage of application, and there is still a considerable distance before they can be practically applied to thermoelectric



Figure 1 Working modes of new electron microscopy techniques. (a) Schematic of the 4D-EELS experimental setup for phonon dispersion curves, with a slot aperture placed parallel to the cBN-diamond interface, producing dispersion diagrams along the Γ - Σ -K-X high-symmetry line [7]. (b) Schematic of the 4D-STEM setup, where a convergent electron beam scans the sample point by point, collecting diffraction patterns to form a 4D-STEM dataset for ptychography [9]. (c) Schematic of the MEMS chip with eight electrical contacts for thermoelectric *in-situ* TEM characterization, with contacts for dual-probe electrical characteristics and two groups of heating elements and temperature sensors [10].

materials. Additionally, electron microscopy techniques for material characterization face limitations such as high costs, operational complexity, and challenges in sample preparation.

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Author contributions

P.N. and B.G. supervised the project. P.N. wrote the manuscript. All authors reviewed and edited the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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