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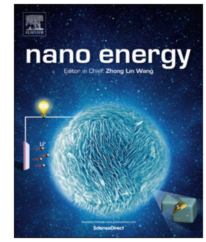

REVIEW

Advanced electron microscopy for thermoelectric materials

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Abstract
Thermoelectric (TE) materials can interconvert waste heat into electricity, thus are promising for power generation and solid-state refrigeration. The thermoelectric properties of a certain material strongly correlate with its chemical, structural and electronic features; therefore, a thorough characterization of these features is not only crucial to profoundly understand the material itself, but also helps to design new materials with desired properties. Under this circumstance, various electron microscopy (EM) techniques are developed, from micro-scale to atomic-scale, two-dimensional (2-D) to 3-D, and static to dynamic. In this review, we review advanced EM techniques already applied in and also look into the perspective of introducing more EM techniques into the field of thermoelectrics. Specifically, we firstly summarize "what have been done" involving: structural and chemical characterizations of all-scale "imperfectness", electronic structure investigation, 3-D morphology and dynamic evolution of nanostructures, and atomic-scale mapping of Seebeck coefficient and defects; based on these characterized features, we then briefly review the calculations on electrical and thermal transport properties to illustrate the structure–property correlations. In what follows, we propose "what can be done" in TEs via EM techniques including: valence-electron distribution, quantitative measurement of atomic displacement, point defect characterization, local band gap measurement, phonon excitation detection, electrostatic potential determination, thermal stability of nanostructures, and in-situ observation and measurement of local TE effects.

Contents

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Introduction

Thermoelectrics

Thermoelectric (TE) effects refer to the mutual induction between a temperature difference and an electric potential. Conceptually, TE devices could be used in power generation and solid-state refrigeration. TE power generation represents a field of energy conversion technology, which can harvest and convert the widely distributed waste heat into electricity; therefore, it is of great potential to relieve worldwide energy shortage. One typical application is to gather electrical power from abundant exhaust gases in next-generation vehicles. TE refrigeration is deemed as an environment-friendly technique, which can be widely applied for small-scale or localized cooling in computers, infrared detectors, electronics, and optoelectronics as well as many other devices. Considering its huge potential in practical applications, TE is a research hotspot in recent fifty years, as shown in Figure 1.

However, the main obstacle between the conceptual TE technologies and practical applications is the unsatisfactory performance of TE materials [1-3]. To date, promising TE materials that have been widely studied typically include either feature as follows: isotropic structures (e.g., PbTe [4-7], PbSe [8], PbS [9,10], SnTe [11], Mg_2Si-Mg_2Sn [12], SiGe [13,14]), anisotropic layered structures (e.g., Bi/Sb_2Te_3 [15,16], In_4Se_3 [17], SnSe [18]; $Ca_3Co_4O_9$ [19,20], BiCuSeO [21]), structures with phase transitions (IVA-VIA: e.g., GeTe [22,23], SnSe [18]; IB_2-VIA: e.g., Cu_2Se [24,25], Cu_2S [26], Ag_2Se [27]; IB-VA-VIA_2: e.g., $AgBiSe_2$ [28-30]), pseudo-cubic structures (IB-IIIA-VIA_2: e.g., $CuGaTe_2$ [31,32], $GuInTe_2$ [33]), superionic structures (e.g., Zn_4Sb_3 [34,35], Cu_2Se [24,25],

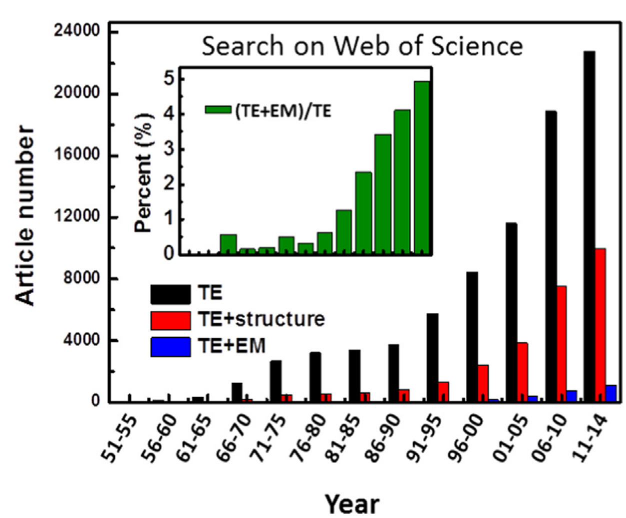

Figure 1 The number of Published articles on TEs as a function of date: The data is based on statistics from Web of Science. The search topic is "thermoelectric, TE", "thermoelectric and structure, TE+structure" and "thermoelectric and electron microscopy, TE+EM".