Fast ion transport for synthesis and stabilization of $\beta$-Zn$_4$Sb$_3$

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Mobile ion-enabled phenomena make $\beta$-Zn$_4$Sb$_3$ a promising material in terms of the re-entry phase instability behavior, mixed electronic ionic conduction, and thermoelectric performance. Here, we utilize the fast Zn$^{2+}$ migration under a sawtooth waveform electric field and a dynamical growth of 3-dimensional ionic conduction network to achieve ultra-fast synthesis of $\beta$-Zn$_4$Sb$_3$. Moreover, the interplay between the mobile ions, electric field, and temperature field gives rise to exquisite core-shell crystalline-amorphous microstructures that self-adaptively stabilize $\beta$-Zn$_4$Sb$_3$. Doping Cd or Ge on the Zn site as steric hindrance further stabilizes $\beta$-Zn$_4$Sb$_3$ by restricting long-range Zn$^{2+}$ migration and extends the operation temperature range of high thermoelectric performance. These results provide insight into the development of mixed-conduction thermoelectric materials, batteries, and other functional materials.
Mass transport, along with energy and charge transfer, is ubiquitous in nature and underscores diverse phenomena in science, engineering, and technology. Ionic migration is an important form of mass transport. On the one hand, electric field-driven ionic migration enables a wide range of applications such as batteries, fuel cells, and sensors. On the other hand, ionic migration risks phase instability, for example, precipitation occurs when the mobile ion’s electrochemical potential is higher than its atomic counterpart. For the sake of phase stability, the voltage across an ionic conductor needs to be lower than the material-specific temperature-dependent threshold.

Here arise two profound questions. First, whether the mass transport in the form of ionic migration can be utilized towards fast materials synthesis. Mass transport mechanisms, different from the traditional thermal diffusion, are a frontier topic of materials science and engineering. Second, whether the interplay between mobile ions, thermal, and electric fields can yield certain microstructures that stabilize the phase at a level beyond the aforementioned “threshold.”

$\beta-Zn_{4}Sb_{3}$ is a perfect material template to address these questions. $\beta-Zn_{4}Sb_{3}$ is known for its complex crystal structure as well as the coexistence of mixed electronic and ionic conduction and promising thermoelectric (TE) performance in the low to intermediate temperature range (400–700 K).

Unlike most state-of-the-art TE materials that are electron-based semiconductors or semimetals, the mobile ions in $\beta-Zn_{4}Sb_{3}$ play a vital role in its promising TE performance in the context of the Electron-Crystal Phonon-Liquid paradigm. The weakly bonded Zn interstitials enable highly mobile $Zn^{2+}$ and also ultra-low thermal conductivity. However, broader commercial applications of $\beta-Zn_{4}Sb_{3}$ face two long-standing obstacles: developing time- and cost-efficient synthesis recipes and maintaining good phase stability while delivering outstanding TE performance.

To overcome these two $\beta-Zn_{4}Sb_{3}$-specific obstacles and to answer the two aforementioned general questions, here we have utilized the fast migration of $Zn^{2+}$ ions under electrical field and a dynamical growth of three-dimensional (3D) ionic conduction network to attain ultra-fast synthesis of $\beta-Zn_{4}Sb_{3}$. The presence of an electric field and the dynamic formation of 3D ionic conduction network speeded up the mass diffusion process and the chemical reaction of Zn and Sb into $\beta-Zn_{4}Sb_{3}$ compared to the typical temperature-driven diffusion and chemical reactions. Due to the rapid cooling of the ion channel bulge when the current is cut off, the amorphous nonstoichiometric $Zn_{n}Sb_{n}$ layer is formed and encapsulates crystalline $\beta-Zn_{4}Sb_{3}$ grain. Such a core-shell crystalline-amorphous micromorphology, especially the amorphous grain boundary, restricts the migration of $Zn^{2+}$ ions across grains, and thus suppressed Zn precipitates. Hence, the as-formed core-shell microstructures self-adaptively suppress the thermodynamic re-entry instability of $\beta-Zn_{4}Sb_{3}$. Finally, doping by Cd or Ge on the Zn site as a steric hindrance further inhibits the migration of $Zn^{2+}$ ions within each grain. All these mechanisms worked jointly to improve the phase stability of $\beta-Zn_{4}Sb_{3}$ and extend the operating temperature range of high TE performance.

**Robust properties.** $\beta-Zn_{4}Sb_{3}$ is a high-performance TE material made of cheap and relatively nontoxic elements. TE materials directly convert heat into electricity through the Seebeck effect, or function as heat pumps via the Peltier effect, thereby playing an important role in our global package of renewable energy options. The efficiency of a TE material is gauged by its dimensionless figure of merit ZT, defined as $ZT = \alpha^2T(\kappa_e^{-1} + \kappa_i^{-1})$, where $\alpha$, $\kappa_e$, $\kappa_i$, and $T$ are the Seebeck coefficient, electrical conductivity, lattice thermal conductivity, electronic thermal conductivity, and the absolute temperature, respectively. The detailed TE transport measurements of the $Zn_{n}Sb_{n}$-based samples were performed, as shown in Supplementary Figs. 4–12. The EFAS $Zn_{n}Sb_{n}$-based compounds show excellent TE performance. For the EFAS $Zn_{1.96}Cd_{0.04}Sb_{3}$ sample, the maximum ZT value of 1.2 is achieved at 693 K (cf. Supplementary Fig. 7), while for the EFAS $Zn_{1.97}Ge_{0.03}Sb_{3}$ sample, the maximum ZT value of 1.12 is achieved at 700 K (cf. Supplementary Fig. 10). Upon doping with Cd or Ge, the overall ZT value increases in comparison with that of the pristine $Zn_{4}Sb_{3}$ sample in the entire range of temperatures (cf. Supplementary Figs. 7 and 10).

In history, the promising TE performance of $\beta-Zn_{4}Sb_{3}$-based compounds is overshadowed by the phase instability between 425 and 565 K, and also the severe ion migration and Zn precipitates (kinetics instability) under an applied electric field even at room temperature (cf. Supplementary Fig. 13). For example, the MQ + SPS $Zn_{4}Sb_{3}$ sample shows very different TE properties when measured twice, and the sample undergoes irreversible change during the measurement (cf. Supplementary Fig. 14).
In contrast, the electrical conductivity, Seebeck coefficient, thermal conductivity, and calculated ZT curves of the EFAS Zn₄Sb₃-based compounds are very repeatable and reproducible (cf. Supplementary Figs. 15–20). The room temperature electrical conductivity of all the samples before and after a test cycle is presented in Fig. 1d. It is obvious that the electrical conductivity of the MQ + SPS Zn₄Sb₃ sample decreased significantly from $6.7 \times 10^4$ to $4.4 \times 10^4$ Sm⁻¹, and that of EFAS Zn₄Sb₃ sample decreased slightly from $5.9 \times 10^4$ to $5.8 \times 10^4$ Sm⁻¹, while that of EFAS Zn₃₋₀.₀₆Cd₀.₀₄Sb₃ sample and that of EFAS Zn₃.₉₇Ge₀.₀₃Sb₃ sample remain almost unchanged at about $5.3 \times 10^4$ to $5.4 \times 10^4$ Sm⁻¹, respectively.

We also measured the Zn²⁺ conductivity and ran endurance tests under high current density at elevated temperatures. We employed a direct-current (DC) polarization method with electron-blocking electrodes to isolate the ionic conduction by filtering out the electronic conduction. Commercial zincloaded montmorillonite served as the electrodes. As shown in Supplementary Fig. 21, the Zn²⁺ migration rate is found to be $3.3 \times 10^{-3}$ Sm⁻¹ at room temperature by the alternating-current (AC) electrochemical impedance spectroscopy (EIS). Solid-state Au|zinc-loaded montmorillonite[Zn₄Sb₃]-based compounds|zinc-loaded montmorillonite/Au pseudo-galvanic cell was constructed (cf. Supplementary Fig. 22), in which all Zn₄Sb₃-based samples have a similar size of $8 \times 8 \times 1.3$ mm³. When the output voltage is close to 10 V, which is the device limit, the current is reduced from 25 μA in the MQ + SPS Zn₄Sb₃, to 3.5 μA in the EFAS Zn₄Sb₃, to 1.9 μA in the EFAS Zn₃₋₀.₀₆Cd₀.₀₄Sb₃, and finally to <1.9 μA in the EFAS Zn₃.₉₇Ge₀.₀₃Sb₃, as shown in Supplementary Figs. 23–26. The room temperature ionic conductivities of MQ + SPS Zn₄Sb₃, EFAS Zn₄Sb₃, EFAS Zn₃₋₀.₀₆Cd₀.₀₄Sb₃, and EFAS Zn₃.₉₇Ge₀.₀₃Sb₃ samples were calculated to be $5.9 \times 10^{-5}$, $7.5 \times 10^{-6}$, $4.5 \times 10^{-6}$, and $4.2 \times 10^{-6}$ Sm⁻¹, respectively (cf. Fig. 1e). Hence, the Zn²⁺ conductivity in the EFAS samples is suppressed by an order of magnitude compared to the MQ + SPS sample, which partially explains the observed improvement in the phase stability and the reproducibility of transport data.

Doping Cd or Ge further enhanced the phase stability as evidenced by the results of electromigration tests conducted at a temperature of 473 K, a DC current density of 20 A/cm², and a charging time of 24 h (cf. Supplementary Figs. 27 and 28). For comparison, the electromigration test was also carried out on the MQ + SPS sample under the same conditions. Supplementary Figs. 29–32 show the fracture surface morphology of typical samples after the electromigration tests. Obious cracking and precipitation of Zn whiskers are observed on the MQ + SPS sample (cf. Supplementary Fig. 29). In contrast, the grain surface of the EFAS Zn₄Sb₃ sample only becomes rough with no discernible precipitation of Zn (cf. Supplementary Fig. 30), and the grain surface of the EFAS Zn₃₋₀.₀₆Cd₀.₀₄Sb₃ sample is very clean with only a small number of microcracks (cf. Supplementary Fig. 31). Even better results are obtained with the EFAS Zn₃.₉₇Ge₀.₀₃Sb₃ sample, which shows no cracks but a clean surface (cf. Supplementary Fig. 32).

The above results corroborate that the chemical stability of the EFAS samples is greatly improved. Combined with doping at the Zn sites, particularly doping with Ge, makes the EFAS samples exceptionally stable even under a high DC electric field. In the following sections, we will pinpoint the microscopic origins of the phase formation and the phase stability.

**Fig. 1 Ultra-fast synthesis, composition, and properties of β-Zn₄Sb₃-based materials.** a Schematic diagram of the reaction apparatus, “1–4” represents the DC pulse power supply, graphite die, BN layer, stoichiometric admixture of Zn and Sb powders, respectively. b Time profile of the reaction parameters, including the loading pressure, temperature of the admixture, displacement of the graphite punch, current, voltage, and sintering function (i.e., the derivative of displacement). c Phase composition of the synthesized samples (standard XRD spectra of PDF#01-089-1969). d Room temperature electrical conductivity of MQ + SPS Zn₄Sb₃, EFAS Zn₄Sb₃, EFAS Zn₃₋₀.₀₆Cd₀.₀₄Sb₃, and EFAS Zn₃.₉₇Ge₀.₀₃Sb₃ samples before and after a test cycle; “A” and “Z” represent the sample at the beginning and end of the electrical conductivity test. e Room temperature Zn²⁺ ionic conductivities of MQ + SPS Zn₄Sb₃, EFAS Zn₄Sb₃, EFAS Zn₃₋₀.₀₆Cd₀.₀₄Sb₃, and EFAS Zn₃.₉₇Ge₀.₀₃Sb₃ samples (orange arrow indicating the decline of ionic conductivity).
Phase formation mechanism. To pinpoint the phase formation mechanism of β-Zn₄Sb₃ in the EFAS process, we first need to differentiate the effect of heating (nondirectional) and the effect of electric field (directional). Specially, we pay close attention to two specific aspects:

Aspect #1 Temporal window of phase formation.
Single phased β-Zn₄Sb₃ can be obtained within 60 s under a pulsed DC field. However, when the charging time extends past 83 s (cf. Supplementary Fig. 33), it is observed that ZnSb forms at the upstream side of the sample, and Zn whiskers precipitate at the sample’s downstream side. We invert the die and the sample (turned upside down) and charge for 18 s (cf. Supplementary Fig. 34), the Zn and ZnSb are gone, and a homogeneous β-Zn₄Sb₃ sample re-emerges. These observations corroborate that (i) the as-formed β-Zn₄Sb₃ serves as a fast transport channel of Zn²⁺ ions, and (ii) there is a temporal window for the phase formation of β-Zn₄Sb₃, beyond which the decomposition occurs in the presence of an electric current.

Aspect #2 The process of phase formation.
The phase formation of β-Zn₄Sb₃ is the result of the competition between field-assisted phase formation and phase decomposition. Figure 2a depicts a number of intermediate stages in the process of phase formation of β-Zn₄Sb₃. More detailed experimental results are provided in Supplementary Fig. 41. When Zn and Sb powders are in physical contact, a small amount of β-Zn₄Sb₃ is formed under the pulsed electric field within less than 10 s, the process is controlled by mutual inter-diffusion of Zn and Sb. Between 10 and 36 s, both the amount of ZnSb and β-Zn₄Sb₃ increase simultaneously, as reflected by the peak in the sintering function curve in Fig. 1b. The appearance of ZnSb suggests that the transport speed of Zn²⁺ ions is so fast in the ion channels of β-Zn₄Sb₃ that Zn cannot be replenished in a timely manner so some are as-formed β-Zn₄Sb₃ decomposes back into ZnSb and Zn. Then, the amount of ZnSb gradually decreases while that of β-Zn₄Sb₃ further increases, which reflects the fact that the as-formed β-Zn₄Sb₃ forms a 3D network and makes more Zn available to react with ZnSb into β-Zn₄Sb₃. Finally, β-Zn₄Sb₃ is attained at the time of 56 s.
The microstructural evolution confirms that the as-formed β-Zn₄Sb₃ serves as a fast transport channel of Zn²⁺ ions, first form nuclei, and crystals, and then form a 3D network, through which Zn²⁺ can be transported quickly under the electric field (cf.
Phase stability mechanism. The core-shell crystalline-amorphous micromorphology somewhat explains the observed improvement of chemical stability of the EFAS samples because the amorphous layer is not ionic conducting. More details are provided by the in situ transmission electron microscopy study. The responses to an electric field applied to MQ + SPS Zn4Sb3 sample and EFAS Zn4Sb3 sample are recorded in detail in the Supporting information (cf. Supplementary Movies 1 and 2).

In addition, Fig. 4a–f shows different stages (in time) when the current flows through the EFAS Zn4Sb3 sample. When the applied voltage exceeds 0.69 V, the grain boundary is gradually widened, increasing from ~20 to ~74 nm, and, finally, the grain collapses and the material becomes unstable. Figure 4g–i shows the high-angle annular dark-field (HAADF) image and its corresponding energy-dispersive X-ray spectroscopy (EDS) spectrum of the EFAS Zn4Sb3 sample after the current is turned off. It is obvious that the Zn2+ ions migrate downstream along the current, and the upstream grains crack and fragment due to the loss of Zn. Fine structures of the grain boundary were studied (cf. Fig. 4j–l). White particles, aka Zn metal, are precipitated at the junction of the two grains (cf. Fig. 4l) and are amorphous (cf. Fig. 4k).

Interestingly, the surrounding areas of the white precipitates become crystalline. Apparently, when the applied voltage on the material is higher than the critical voltage, the amorphous grain boundary crystallizes into β-Zn4Sb3, which conducts Zn2+ ions under the electric field and finally destabilizes the grain. On the contrary, as long as a voltage is applied, the grains of MQ + SPS Zn4Sb3 sample will crack and disintegrate continually, and there is no phenomenon of grain boundary widening (cf. Supplementary Fig. 45 and Supplementary Movie 2).

Figure 5 shows the schematic diagram of β-Zn4Sb3 microstructure derived by different synthesis methods. For MQ + SPS Zn4Sb3 sample, ion channels run through the grains to the entire bulk as there is no ion migration blocking mechanism (cf. Fig. 5a). While for the EFAS Zn4Sb3 sample, ion channels are limited to the interior of the grain, and the amorphous layer on the contact point between Zn and Sb particles when the current is loaded (6 s). c β-Zn4Sb3 crystal grows up gradually, and the composition in the upstream region of the current is poor in Zn, while the composition in the downstream region is rich in Zn (12 s). d β-Zn4Sb3 3D network is formed as growing β-Zn4Sb3 crystals contact each other (36 s). e Special grain boundary network structure filled with a large number of β-Zn4Sb3 nanocrystals is formed due to the ion channel bulge. f Core-shell microstructure consisted of crystalline β-Zn4Sb3 grains and amorphous off-stoichiometric Zn4Sb3 grain boundaries that are formed when the current is off.

Figure 2b–f. Finer microstructure details of β-Zn4Sb3 were investigated by TEM (cf. Figure 2g–i). The crystal grain shows a perfect β-Zn4Sb3 lattice, while the grain boundary appears to be amorphous. The amorphous grain boundary located at the downstream side of current is rich in Zn (cf. Fig. 2h), while the counterpart at the upstream side of current is poor in Zn (cf. Fig. 2i), de facto forming a special core-shell structure composite.

These results point toward a schematic diagram of the reaction mechanism as shown in Fig. 3a–f. When Zn is in physical contact with Sb, under the pulse current, β-Zn4Sb3 nuclei forms (cf. Fig. 3b). Due to the high ionic conductivity of Zn2+ in β-Zn4Sb3, Zn2+ ions are easily transported through the as-formed β-Zn4Sb3 and react with Sb forming additional β-Zn4Sb3 in spite of Zn being separated from Sb by β-Zn4Sb3 (cf. Fig. 3c). Due to the transport speed of Zn2+ in the ion channel of β-Zn4Sb3 mismatches the local supply of fresh Zn, the upstream and downstream side of grain boundaries tend to be, respectively, poor and rich in Zn along the current direction. As β-Zn4Sb3 crystals contact each other (at ~36 s), a 3D network is formed (cf. Figure 3d), which greatly promotes the transport speed and scope of Zn2+ ions and makes β-Zn4Sb3 grains grow rapidly. In particular, a large number of β-Zn4Sb3 nanocrystals are formed at the ion channel bulges, these nanocrystals fill the voids between Zn4Sb3 grains, and lead to the densification of material (cf. Fig. 3e). Normally, the current discharge at the grain boundary produces highly intensive Joule heating. When the current is off, the rapid cooling at the contact quenches nanocrystals to amorphous, forming the core-shell crystalline-amorphous microstructure (cf. Fig. 3f).
the grain boundary (respectively, poor and rich in Zn) blocks the formation of the network due to the lack of ion channels, so as to improve the stability of the bulk material (cf. Fig. 5b). Moreover, the literatures 5,37,38 show that foreign elements can replace dynamic Zn, and thus reduce the ionic conduction and thus improve the stability. To sum up, the core-shell crystalline-amorphous microstructure combined with doping by foreign elements (i.e., Cd or Ge) at the Zn sites inhibit the migration of dynamic Zn$^{2+}$ ions at multiple scales, and improve the thermodynamic (phase transition, cf. Supplementary Figs. 43 and 44) and kinetic (ionic migration, cf. Supplementary Figs. 29–32) stability of $\beta$-Zn$_4$Sb$_3$.

**Fig. 4** In situ microstructure evolution. a–f Different stages (in time) during the current flow through the EFAS Zn$_4$Sb$_3$ sample (the grain boundary reaches the widest at the $N_0$ frame). g–i The HAADF image and the corresponding EDS spectrum of EFAS Zn$_4$Sb$_3$ sample after the current are turned off. j Enlarged HAADF image of the grain boundary area delineated by an orange border in (g); white particles are precipitated at the junction of the two grains. k–l High-resolution images and EDS spectra of white particles.
In summary, we have prepared a series of $\beta$-Zn$_3$Sb$_3$-based compounds with different dopants by an EFAS technique. The mechanism of phase formation and decomposition, and chemical stability, along with the TE transport properties, have been discussed in detail. Under the DC electric field, the ion transport channel in $\beta$-Zn$_3$Sb$_3$ enables fast mass transport and participates in chemical reactions. A dense EFAS $\beta$-Zn$_3$Sb$_3$-based bulk material can be formed within 60 s. The resulting bulk composite material has a crystal-amorphous core-shell micromorphology. The as-formed composite microstructure, in conjunction with Cd/Ge doping, stabilizes the high TE performance of $\beta$-Zn$_3$Sb$_3$ via suppressing the long-range Zn ions migration and precipitates of Zn on the grain boundaries. Specifically, the Zn$_{2+}$ ionic conductivity is decreased by more than an order magnitude from $5.9 \times 10^{-3}$ Sm$^{-1}$ for the MQ + SPS sample to $4.2 \times 10^{-6}$ Sm$^{-1}$ for the Ge-doped structure. Moreover, $\beta$-Zn$_3$Sb$_3$ was doped with 0.75 at.% Ge shows essentially no change when carrying the current density of 20 A/cm$^2$ at 473 K for 24 h. The Cd-doped structure Zn$_{3.96}$Cd$_{0.04}$Sb$_3$ attained $ZT_{\text{max}} = 1.2$, at 693 K, while the Ge-doped Zn$_{3.97}$Ge$_{0.03}$Sb$_3$ sample reached $ZT_{\text{max}} = 1.12$, at 700 K. The synthesis method can be in principle extended to, for example, ZnSb, Cu$_2$Se, and Cu$_2$S (cf. Supplementary Figs. 46–48), which is of great technical implications.

Methods

Synthesis. Four grams of Zn (5N, 200 mesh) and Sb (5N, 200 mesh) or Cd (5N, 200 mesh) and Ge (5N, 200 mesh) powders were weighed according to the stoichiometric ratio and were thoroughly mixed in an agate mortar for 20 min. The mixed raw powders were transferred into the mold (Φ16 mm) in Fig. 1a. The inner wall of the graphite mold was coated by a layer of BN to ensure most current flow through the powder admixture. A thermocouple was inserted into the admixture to measure the reaction temperature. In a typical process, a vacuum level ≤ 20 Pa was maintained. Next, a pulsed sawtooth-shaped current is applied to the mold for 60 s. The resulting pellet with a diameter of 16 mm and a height of 3 mm had a relative density of more than 98%. The ingot was cut into appropriate shapes for the TE property measurements and electromigration tests.

Moreover, the EFAS processes for Bi$_2$Te$_3$, ZnSb, Cu$_2$Se, and Cu$_2$S compounds are really similar.

Test of ionic conductivity of Zn$_{2+}$. The migration rate of Zn$_{2+}$ ions in the commercial zinc-loaded montmorillonite was tested through AC EIS. A solid-state Au(zinc-loaded montmorillonite)/Zn$_3$Sb$_3$-based compounds/zinc-loaded montmorillonite/Au pseudo-galvanic cell was constructed, in which all Zn$_3$Sb$_3$-based samples have a similar size of $8 \times 8 \times 1.3$ mm$^3$. Then, based on the DC polarization measurements, the resulting ionic conductivities of Zn$_3$Sb$_3$ (MQ + SPS), Zn$_3$Sb$_3$ (EFAS), Zn$_{3.96}$Cd$_{0.04}$Sb$_3$ (EFAS), and Zn$_{3.97}$Ge$_{0.03}$Sb$_3$ (EFAS) at room temperature could be obtained.

Chemical electromigration tests. Electromigration tests were conducted at a temperature of 473 K, with the DC current density of 20 A/cm$^2$, and the charging time of 24 h. High-purity argon gas of 100 Pa filled the cavity to avoid a short circuit.

Characterization. The phase purity of all samples was inspected by X-ray powder diffraction (Empyrean, Cu K$_\alpha$, line, PANalytical, Holland). Images of freshly fractured surfaces were taken by field emission scanning electron microscopy (SU8000, Hitachi, Japan) with EDS (XFlash6160, Bruker, Germany). Back-scattered images were taken by EPMIA (JXA-8100, JEOL, Japan). A direct characterization of the samples’ atomic structures and structural evolution during the process of electrophoresis was carried out on transmission electron microscopy (Talos F200s, FEI) and double spherical aberration-corrected transmission electron microscopy (Titan Themis G2 60-300, FEI). The samples for TEM observation were prepared by ion milling with liquid nitrogen (PIPS 695, Gatan) and focused ion beam milling (Helios Nanolab G3 UC, FEI). In situ biasing experiments were performed within the TEM column using a TEM-STM holder (Pico Femto, Zeptodk). The low- and high-temperature heat flow of the Zn$_3$Sb$_3$-based samples, respectively, was detected by Q2000 (TA, USA).

The electrical conductivity ($\sigma$) and the Seebeck coefficient ($\alpha$) were measured simultaneously using a commercial equipment (ZEM-3, Ulvac, Japan). The high-temperature Hall coefficient ($R_H$) was measured in a magnetic performance testing system (NYMS, China), using the van der Pauw method under a reversible magnetic field of 1.5 T. The low-temperature $\sigma$ and $R_H$ between 10 and 300 K were measured on a Physical Properties Measurement System (PPMS-9, Quantum Design, USA). The effective carrier concentration ($n_{\text{eff}}$) was calculated by the formula: $n_{\text{eff}} = 1/eR_H$, where $e$ is the electron charge. The Hall mobility follows $\mu_{\text{H}} = dR_H/d(1/B)$. The thermal conductivity was calculated from the relation $\kappa = D \times c_p \times \rho$, where $D$ is the thermal diffusivity coefficient, $c_p$ is the specific heat capacity, and $\rho$ is the bulk density. $D$ was measured using an LFA437 (Netzsch, Germany) laser flash apparatus. $c_p$ was taken as the Dulong–Petit law value. $\rho$ was obtained by the Archimedes method.

Data availability

The authors declare that all data supporting the findings of this work are available from the corresponding authors upon reasonable request.

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Author contributions
D.Y. and X.T conceived this work. D.Y., X.S., Y.Yan and Y.L. prepared the materials and tested their TE performance; D.Y. and J.L. tested the ionic conductivity of ZnSb: D.Y. did the chemical electromigration tests; H.B., T.L., H.L., Y.Yu and J.W. carried out the TEM experiment and analyzed the data; D.Y., J.H., Q.Z. and C.U. analyzed the experimental data; D.Y., J.H. and X.T. cowrote the manuscript. All authors reviewed, discussed, and approved the results and conclusions.

Competing interests
The authors declare no competing interests.

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