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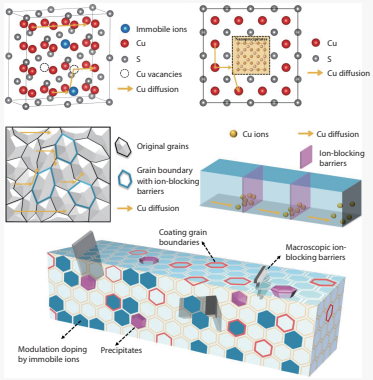
PERSPECTIVE

Materials Lab 2024, 3, 230017

The stability of copper sulfides thermoelectric materials

Yi-Xin Zhang and Zhen-Hua Ge*

The stability of thermoelectric materials is critical in determining their suitability for commercial device applications. Copper sulfides are superionic conductors with highly disordered Cu ions, which results in exceptional thermoelectric properties at high temperature. However, this feature also causes unbalanced Cu ions concentration as well as the poor service stability under external fields. Researchers are focusing on enhancing the service stability of copper-based superionic conductors. This perspective reviews the mechanisms of Cu ions migration, metal deposition, and materials degradation of copper sulfides. The importance of appropriately inhibiting long-range migration of Cu ions is emphasized. Based on an analysis of the effects of multiple scaled ion-blocking barriers on ion, carrier and phonon transportation, some rational approaches for improving service stability of copper sulfides while maintaining their thermoelectric performance are proposed, which would increase the possibility of utilizing copper sulfides in thermoelectric device applications.



Thermoelectric (TE) technology, capable of directly and reversibly converting temperature gradient into electricity and vice versa, has intrigued widespread interests in the field of waste heat harvest, particularly for distributed waste heat sources, such as automobile exhaust heat, solar light heat, and low quality geothermal heat[1-3]. TE devices have high flexibility, reliability and emit no pollutants, making them commercially competitive if their thermoelectric performance and service stability can be improved[4-6]. Thermoelectric conversion efficiency is determined by the dimensionless figure of merit, $ZT=\alpha^2\sigma T/\kappa$, where α, σ, T, κ represent the Seebeck coefficient, electrical conductivity, absolute temperature (in Kelvin) and total thermal conductivity, respectively. Efforts have been devoted into thermoelectric performance enhancement in the past decades, resulting in ZT values beyond 2.0 in various materials, which were once considered rare[7, 8]. In addition to service stability, maintaining stable phase structures and thermoelectric properties over a long period of time under specific temperature gradients without any degradation or structural collapse are crucial for the practical use in various thermoelectric applications[9, 10]. Improving thermal and electrical stability often involving compositional and structural adjustment, which can affect the carrier and phonon transport. Therefore, a significant research emphasis is on improving service stability while maintaining excellent thermoelectric performance, particularly for materials with complex crystal structures and dynamic ions.

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Received 4 April 2023; Accepted 14 May 2023; Published online

$Cu_{2-x}S$-based superionic conductors

This perspective takes copper sulfides ($Cu_{2-x}S$, $0\le x\le 0.25$) as example to introduce some rational strategies for improving service stability of superionic conductor thermoelectric materials. Copper sulfides are a series of compounds with similar composition but different structures, including monoclinic low-chalcocite (Cu_2S)[11], monoclinic djurleite ($Cu_{1.93\text{-}1.97}S$)[12], triclinic roxbyite ($Cu_{1.81}S$)[13], cubic digenite ($Cu_{1.8}S$)[14], orthorhombic anilite ($Cu_{1.75}S$)[15]. The crystal structure of $Cu_{2-x}S$ depends on temperature, stoichiometry, and synthesis conditions[16, 17]. At high temperature, $Cu_{2-x}S$ has a cubic structure with a space group of *Fm-3m*, where S atoms construct the rigid *FCC* sub-lattice of the material, while Cu ions are highly disordered in the framework, greatly scattering the phonon propagation and even reducing part of transverse vibrational modes, leading to ultralow lattice thermal conductivity[18]. Additionally, lowering the Cu content can change the crystal structure, the phase transition temperature, and the position of valence band maximum, affecting carrier concentration and electrical transport properties[19]. In the past decades, researchers have been optimizing thermoelectric performance using various approaches, such as nanostructuring, band engineering, lattice softening and entropy engineering, ZT beyond 2.0 is also realized in copper sulfides at middle temperature (Fig. 1)[11, 14, 20-53]. The concept of "phonon-liquid electron–crystal (PLEC)" interprets the superior thermoelectric properties of copper sulfides[18]. However, copper-based superionic conductors (Cu_2S, Cu_2Se, $CuAgSe_2$, $CuCrSe_2$) have poor ser-

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DOI: 10.54227/mlab.20230017

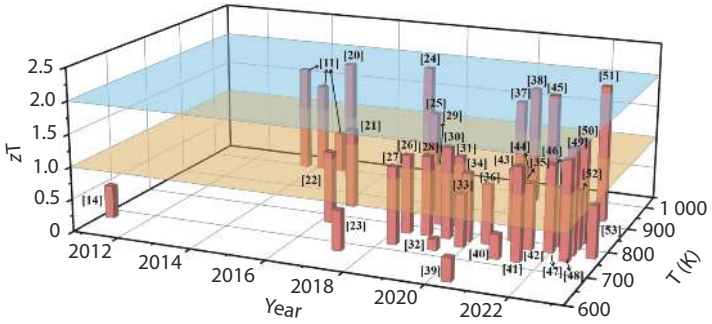


Fig. 1 Dimensionless figure of merit *ZT* for binary copper sulfide-based thermoelectric materials as a function of temperature and year. The data were taken from[11, 14, 20-53].

vice stability due to directional long-range migration of Cu ions in Cu-rich compounds under high current stress or temperature gradients and sulfur framework collapse in Cu-poor compounds at high temperature[54]. Herein, although liquid-like behavior of Cu ions is the key to realizing high TE performance in Cu-based superionic conductors, it also causes poor stability under service conditions.

Electrical stability

The stability of copper sulfides has long been focused. Miyatani et al. observed visible metallic Cu deposition at the cathode of the material when subjected a large current[55]. Dennler et al. synthesized a series of copper sulfides and characterized their electrical stability in a current density range of 12-48 A cm^{-2}[55]. Cotton-shaped copper whiskers deposit at cathode of Cu_2S under a mild current density of 12 A cm^{-2} during 12 h. By contrast, $Cu_{1.8}S$ and CuS specimens are stable in crystal structure and electrical transport properties under higher current density of 48 A cm^{-2}. Qiu et al. revealed the relationships among ion migration, metal deposition, and material degradation in superionic conductors[54]. As shown in Fig. 2a, Cu ions will migrate along the external driving force when copper sulfides suffer from temperature gradient or electric field, causing a Cu ions concentration gradient in the specimen. When this concentration variation is within the limit of material, a dynamically balanced state is reached, since that the generated opposite diffusion force of the migrated Cu ions would against the external applied force on the Cu ions. In this scenario, Cu will not deposit, and the Cu ions are capable of returning to the originally disordered state when the applied force remove. However, when the external force is large enough, the chemical potential of Cu ions at cathode/cold side increases to the chemical potential of pure metal, copper will deposit (Fig. 2b). In addition, Qiu et al. proposed a parameter of critical voltage (V_c) to evaluate if the local Cu concentration of material reach a threshold to generate deposition when subjecting an external force or field[54]. As depicted in Fig. 2c, V_c of $Cu_{2-x}S$ gradually increases with the increase of Cu deficiencies, indicating that introducing Cu vacancies in the copper sulfides is beneficial for increasing the difficulty for the Cu ions to reach the chemical potential of Cu metal. Unfortunately, *ZT* values also gradually drop when the Cu vacancy content reaches 0.03 since that the excessive carrier concentration would jeopardize the Seebeck coefficient and electronic thermal conductivity of copper sulfides. Nevertheless, there are other means of improving V_c while maintaining high *ZT*, such as introducing immobile Fe ions in both $Cu_{1.8}S$ [33] and $Cu_{1.9}S$ [37], the electrical stability and TE performance are simultaneously optimized.

Thermal stability

The thermal stability of $Cu_{2-x}S$ is influenced by various factors, including composition, crystal structure, environmental conditions, and synthesis process. CuS and Cu_2S are thermally stable and can withstand temperatures up to 1273 K without significant decomposition or oxidation. However, some copper sulfides with Cu deficiencies, such as $Cu_{1.8}S$ and $Cu_{1.96}S$, may decompose at temperatures around 673 to 773 K. The sulfur framework is prone to collapse when the copper content falls below the critical value. In such cases, Cu-rich precipitates would deposit on the surface of the sample. This phenomenon typically arises during annealing treatments or high-temperature measurements of $Cu_{2-x}S$ specimens, even in parts of Cu_2S material with lower Cu ion concentration resulting from external fields/force. Moreover, different dopants or composites can either accentuate or weaken the sulfur volatilization at high temperature. For instance, In, Cd, Zn, and Sn doping results in generating a Cu-rich phase at lower annealing temperatures and significant sulfur loss in $Cu_{2-x}S$ materials [45]. Conversely, Pb doping can improve the thermal stability of $Cu_{2-x}S$ as well as significantly enhancing the thermoelectric performance[45]. The relative electrical resistance (R/R_0) of Cu_2S sharply drops at 573 K under a current density of 12 A cm^{-2}, introducing excessive iodine can enhance the electrical stability of copper sulfide (Fig. 2d)[38]. Thus, Cu deficiency is beneficial for reducing the chemical potential of Cu ions, and introducing foreign anions with high electronegativity can reinforce bonding and influence the migration of Cu ions. In addition, suppressing long-range migration of Cu ions is also beneficial for improving thermal stability of copper sulfides, as it maintains local Cu ions concentration and prevents sulfur framework collapse. High current density (48 A cm^{-2}) does not degrade $Cu_{1.8}S$ material, but a temperature of 573 K induces $Cu_{1.96}S$ deposition on the surface of pure $Cu_{1.8}S$ material. Composition variation increases the contact resistance of copper sulfides. By contrast, compositing with insulated boron particles assist to suppress sulfur volatilization and maintain the relative electrical resistance in a long time (Fig. 2e)[47]. Synthesis process also significantly affect the thermal stability of copper sulfides. A long time annealing

DOI: 10.54227/mlab.20230017

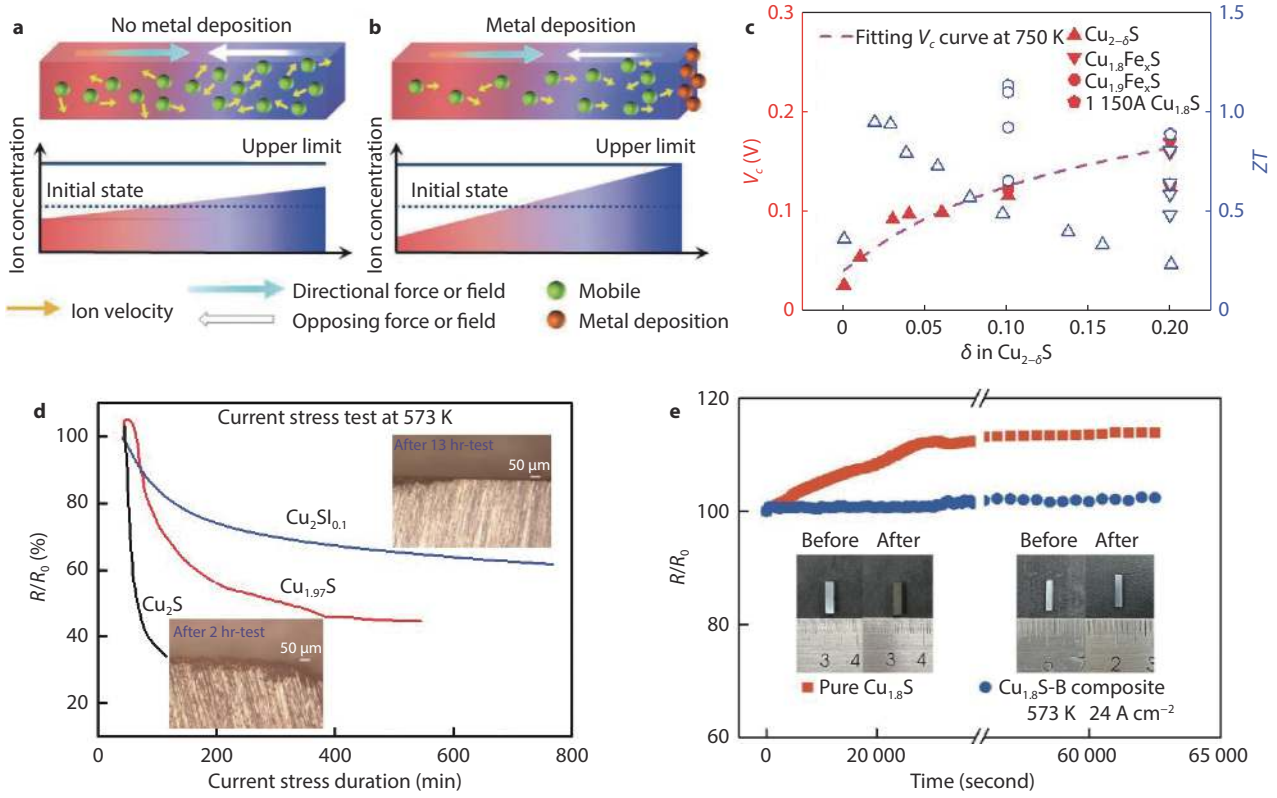


Fig. 2 Schematic of **a** steady state of copper sulfides without ion directional long-range migration (and without metal deposition) and **b** continuous metal deposition (or other decomposition), if the local Cu ion concentration reaches a critical level for the materials[54]. Copyright 2018, Springer Nature. **c** Critical voltage (V_c) and *ZT* at 750 K as a function of Cu vacancy content (δ) for $Cu_{2-\delta}S$ ($0 \le \delta \le 0.2$), $Cu_{1.8}Fe_xS$ (x=0.024, 0.036, 0.048 and 0.064), $Cu_{1.9}Fe_xS$ (x=0.0125, 0.0225 and 0.0325) and high-current SPSed $Cu_{1.8}S$ specimens are included for comparison. **d** Time dependence of relative electrical resistance (R/R_0) for the pure Cu_2S, $Cu_{1.97}S$ and $Cu_2SI_{0.1}$ samples under a large current density (12 A cm^{-2}) at 573 K [38]. Copyright 2020, Elsevier. **e** R/R_0 of $Cu_{1.8}S$ and $Cu_{1.8}S$-B bulk composite as a function of time under a current density 12 A cm^{-2} at 573 K[47]. Copyright 2022, Elsevier.

treatment ensures stable composition and thermoelectric performance, although copper sulfides can be synthesized through various facile approaches, such as mechanical alloying[56], chemical methods[57], or even a very short time vacuum-induced reaction[46]. Among that, spark plasma sintering (SPS) is generally used to fabricate copper sulfide bulk materials. Previous studies also demonstrated that coating BN [58] or using alternating current [59] to avoid high current subjecting the specimens can ensure the material homogeneity.

Strategies for suppressing Cu ion migration

Long-range migration of Cu ions should be reasonably manipulated to optimize service stability while maintaining excellent thermoelectric performance of copper sulfides. Whether the driving force is thermal or electric field, excessive Cu ions concentration at the cathode/or cold side can lead to metal deposition. On the contrary, local lack of Cu ions would cause the sulfur volatilization and Cu-rich precipitates deposition on the surface of materials at high temperature. Compositional and microstructural regulation are regarded as the effective approaches in improving service stability of copper sulfides. Fig. 3 illustrates various scales of ion-blocking barriers in copper sulfides. Among that, Cu vacancies or other immobile ions can decrease the chemical potential of Cu ions, tune the carrier concentration, and scatter short frequency phonons to affect the thermoelectric properties. Nevertheless, the doping limit of most elements in superionic conductors is very low. Therefore, it's necessary to introduce appropriate Cu vacancies to provide more possible sites to be occupied, which is beneficial for increasing hole concentration to reach the optimum range in copper sulfide. On this basis, foreign ions, such as Fe[33], Ni[36] and Mn[52, 53], are easier to enter the lattice of matrix to affect the Cu ions migration, making it more difficult for Cu ions to meet the chemical potential of metallic Cu. Additionally, dispersing nanoprecipitates by in-situ phase separation[60], spontaneous precipitation[61] or mechanical mixing [47] can also improve the electrical and thermal stability of Cu-S and Cu-Se materials. Although these precipitates have different formation mechanisms and locations in the material, they can significantly suppress Cu ions migration to keep local Cu ions concentration. Furthermore, some nanoinclusions, such as CuI[38], B[47] and Ru[42], are favor of suppressing sulfur volatilization, thereby improving thermal stability of $Cu_{2-x}S$ by inhibiting long-range migration of Cu ions. Another proper method is to decorate the grain boundaries as blocking barriers to limit Cu ions motion. For instance, coating a layer of metal on the surface of powders by chemical plating or ion plating can construct interface-scale barriers that block ions but allow electrons to

DOI: 10.54227/mlab.20230017

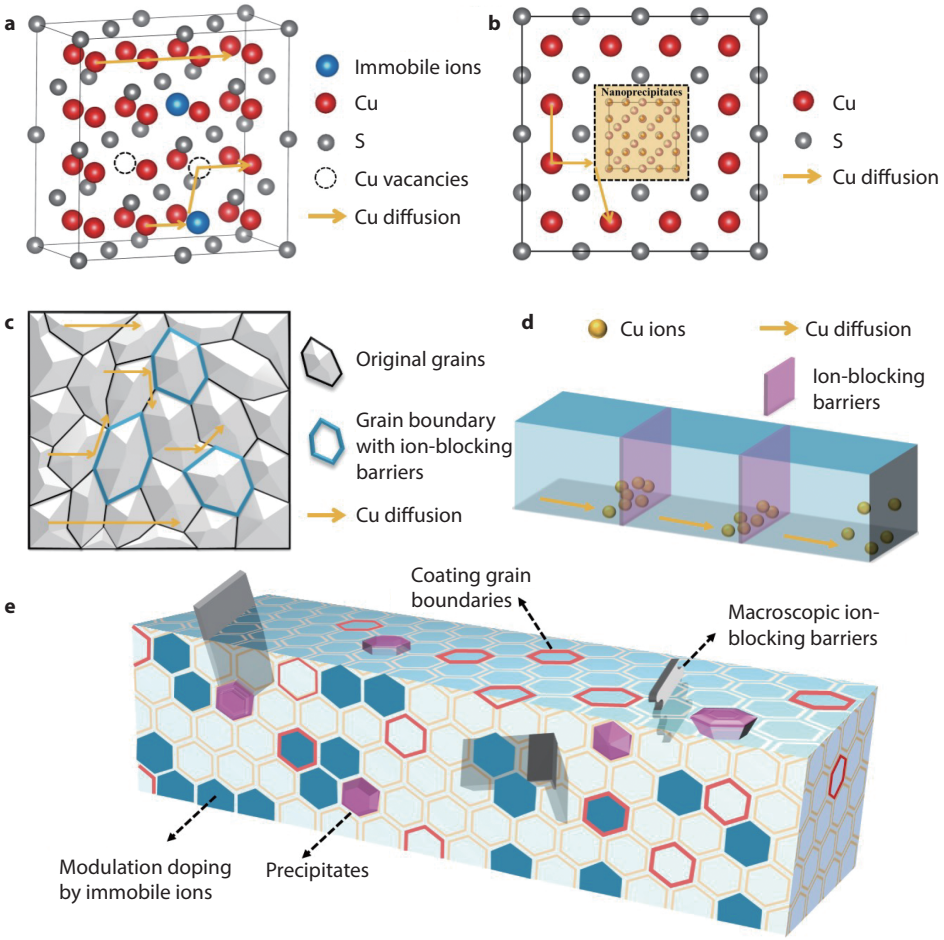


Fig. 3 Multiscale ion-blocking barriers in the copper sulfides. Sketch map of Cu ion diffusion in the framework of copper sulfides at high temperature when **a** atomic-scale defects (immobile ions or Cu vacancies), **b** nanoprecipitates, **c** interfacial scale barriers and **d** macroscopic partition ion-blocking barriers are introduced. **e** Schematic of improving stability of copper sulfides by simultaneously introducing multiscale ion-blocking barriers.

transfer[62]. Then mixing the plated powders with the ordinary powders by referring the concept of modulation doping, benefiting to inhibit Cu ions motion and maintain carrier mobility. It's worth noting that the thickness and content of such barriers should be decent, otherwise, the total thermal conductivity would be greatly increased. The barriers are not necessarily metals, other layers possessing ion-blocking characters, such as semimetals, or even insulators, might also achieve the simultaneous optimization of service stability and thermoelectric performance by strongly hindering ions migration while scattering phonons, especially for the $Cu_{2-x}S$ that has excessive electrical conductivity. On larger scales, using electron-conducting but ion-blocking interfaces between individual segments can limit ion motion inside each segment, in this scenario, the critical voltage of the whole specimen obviously increases with the number of segments[54]. Besides, coating a layer of BN or B_2O_3 on the surface of bulk materials can obviously suppressing the sulfur/selenium volatilization[37]. Therefore, utilizing macroscale ion-blocking barriers to inhibit ions migration and maintain the chemical potential of Cu ions is feasible and effective, which promotes a new strategy to improve service stability of copper sulfides.

Perspectives

This perspective provides a concise overview of the impact of compositional, microstructural and technological modifications on enhancing the service stability of copper sulfides. Various studies highlight the crucial role of maintaining suitable Cu ion concentration in the materials to ensure the stable service of copper sulfides under large electric fields and/or thermal gradients. The key challenges of further advance in copper sulfides or other superionic conductors are decoupling the carrier and phonon transport while maintaining the concentration of disordered ions below the threshold in the materials. One of the primary techniques for tuning the carrier concentration and chemical potential of Cu ions is to regulate the composition by introducing Cu vacancies and/or other immobile ions[63, 64]. In addition, the creation of multiscale ion-blocking barriers using nanoinclusions, interfacial coatings, and macroscopic barriers can further suppress the long-range migration of Cu ions, thereby limiting ion concentration. Some promising barrier materials are worth exploring, such as Al_2O_3, Fe_2O_3, CuO and Cu_2O, and some special microstructures could be constructed, such as heterogeneous stacking structure or building locally magnetic field to affect

DOI: 10.54227/mlab.20230017

the ions migration. Therefore, implementing multiple strategies simultaneously in a single material might be more effective in improving the stability of superionic conductors while preserving their exceptional thermoelectric performance (Fig. 3e). This perspective is only a rough guide for discovering different types, scales, contents and distributions of ion-blocking barriers for optimizing the service stability of materials and facilitating the using of copper sulfides in device applications.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 52162029), Yunnan Provincial Natural Science Key Fund (Grant No. 202101AS070015), National Key R&D Program of China (No. 2022YFF0503804), Outstanding Youth Fund of Yunnan Province (Grant No. 202201AV070005).

■ CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Biographies



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Zhen-Hua Ge is a full professor at Kunming University of Science and Technology. He received his Ph.D. degree in 2013 from University of Science and Technology Beijing, China. And he worked as post-doctoral researcher at University of South Florida and Southern University of Science and Technology from February 2013 to July 2015. His research interests focus on synthesis and properties improvements of thermoelectric materials, especially for sulfides thermoelectric materials.