Blocking Ion Migration Stabilizes the High Thermoelectric Performance in Cu_2Se Composites

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ABSTRACT

The coexistence of fast ionic conduction and high thermoelectric performance in certain mixed ionic-electronic conductors afford new opportunities and challenges beyond the traditional semiconductors and semimetals. However, their applications are limited due to phase instability under a high current density and large temperature difference. Here, we show that the high thermoelectric performance of superionic conductor Cu_2Se is stabilized through regulating the behaviors of Cu^+ ions and electrons in a Schottky heterojunction between the Cu_2Se host matrix and *in situ* formed BiCuSeO nanoparticles. The accumulation of Cu^+ ions via an ionic capacitive effect at the Schottky junction under the direct current modifies space charge distribution in the electric double layer, exerting an electrostatic field, which blocks the long-range migration of Cu^+ and produces a drastic reduction of Cu^+ ion

migration in the composite by nearly two orders of magnitude. Moreover, this heterojunction impedes electrons transferring from BiCuSeO to Cu_2Se, obstructing the reduction reaction of Cu^+ into Cu metal at the interface and hence stabilizes the β-Cu_2Se phase under a high DC current density and/or a large temperature gradient. Furthermore, incorporation of BiCuSeO in Cu_2Se optimizes the carrier concentration and intensifies phonon scattering, contributing to the peak figure of merit ZT value of ~ 2.7 at 973 K and high average ZT value of ~1.5 between 400 K and 973 K for the Cu_2Se/BiCuSeO composites. This discovery thus provides a new avenue for stabilizing mixed ionic-electronic conduction thermoelectrics, and fresh insights into controlling ion migration in these ionic transport dominated materials including perovskite photovoltaic materials, solid electrolytes, and solid state batteries.

One sentence summary: The space charge region in the Schottky junction between the Cu_2Se host matrix and *in situ* formed BiCuSeO under a direct current causes drastic suppression of Cu^+ ion migration in the composites, and obstructs the reduction reaction of Cu^+ into Cu metal, which, together with the effective regulation of carrier concentration as well as enhanced interfacial phonon scattering, greatly stabilizes the improved thermoelectric performance.

1. INTRODUCTION

Thermoelectric (TE) materials allow direct solid-state conversion between heat and electricity via the Seebeck and Peltier effects[1, 2]. Compared to other energy conversion technologies, thermoelectricity has unique technical merits, such as high reliability, long life, and absence of noise or greenhouse emissions, and finds applications in harvesting industrial waste heat, solar energy, ocean or geothermal energy, heat from automobile exhausts, in powering the deep space probes, as well as managing spot-size distributed cooling of electronic devices and household appliances[3]. To date, TE conversion is mainly driven by the development of higher performing, practically stable, and environmentally friendly TE materials. The major scientific and technological challenge is to compete successfully with the established energy conversion technologies and broaden the range of industrial applications of thermoelectricity. The efficiency of a TE material is gauged by its dimensionless figure of merit ZT, defined as $ZT = \alpha^2\sigma T/(\kappa_L+\kappa_e)$, where α, σ, κ_L, κ_e, and T are the Seebeck coefficient, electrical conductivity, lattice thermal conductivity, electronic thermal conductivity, and the absolute temperature, respectively[1].

Among various classes of TE materials, mixed ionic-electronic conductors, such as $Cu_2Te/Cu_2Se/Cu_2S$[4-10], Zn_4Sb_3[11, 12], $Ag_2Te/Ag_2Se/Ag_2S$[13-17], $AgCrSe_2/CuCrSe_2$[18, 19], Ag_8MX_6 (M=Sn, Ge, Si; X=Te, Se, S)[20-22], and Ag_9AlSe_6/Ag_9GaSe_6[23-25], constitute a unique

family[26]. In the mixed conductors, ionic migration coexists with high TE performance in the same temperature regime, indicating an inherent link between the two. In the context of the phonon-glass electron-crystal (PGEC) and hybrid-crystal paradigms of the TE materials research, the mobile ions induce static and dynamic disorders causing strong disruptions of phonon spectra and phonon propagation, and give rise to a "phonon-liquid" behavior[4]. Meanwhile, the non-mobile rigid sub-lattice constitutes the conduction path for electrons or holes, resulting in an electron-crystal behavior. Attaining high TE performance in mixed ionic-electronic conductors entails a delicate balance among mobile ions, conduction electrons, and lattice phonons. Yet, while the mobile ions play a constructive role in suppressing the lattice thermal conductivity, they also reveal their destructive influence by undermining the stability of the structure under large electric fields or temperature gradients. Given that a large current density and temperature gradient are indispensable for efficient TE power generation and refrigeration, achieving high TE performance while maintaining high structural integrity remains a formidable challenge for applications of mixed conduction thermoelectrics.

Because of their environmental friendliness, low cost of raw materials and high TE performance, Cu_2Se and its derivatives are among the most notable mixed conductor systems. The early studies of Cu_2Se-based compounds date back to the 1960s, when the 3M

Corporation developed and patented $Cu_{1.97}Ag_{0.03}Se$ as a potentially promising TE material[27], the variants of which were tested by other research institutions, including General Atomics Corporation[28], Teledyne[29] and the NASA's Jet Propulsion Laboratory[30, 31]. In recent years, more in-depth and systematic studies have been reported on Cu_2Se with the aim of optimizing its TE performance[5, 6], improving its chemical stability[32], and developing new synthesis recipes[7]. Still, the high mobility of Cu^+ ions pose a serious risk to the stability of the material under service conditions that involve high voltage and large thermal gradients. The resulting Cu metal precipitates in the samples and the concomitant structural changes lead to a rapid deterioration of the TE performance, which is the reason why research into the TE prospect of Cu_2Se was once abruptly abandoned[33, 34]. Currently, researchers are keen to find ways to inhibit the long-range migration of Cu^+ and thus improve the material's stability. According to the recent work by Qiu *et al.*[35, 36], it is the material-specific chemical potential difference that governs the precipitation of Cu. Consequently, keeping the operational condition of Cu_2Se below a certain voltage threshold seems to be a safe yet passive and ultimately unsatisfactory solution.

Should the long-range migration of Cu^+ ions be actively inhibited and the carrier concentration self-regulated, Cu_2Se-based materials would have not only excellent TE performance but also good phase stability. This would be extremely conducive to the

commercial applications of Cu_2Se. In this study, by *in situ* forming BiCuSeO nanoparticles in Cu_2Se, the Cu^+ ion modulated electric double layer in the space charge region due to an ionic capacitive effect in the Schottky junction of Cu_2Se/BiCuSeO interface under the direct current effectively blocks the long-range migration of Cu^+ ions throughout the entire sample and hinders the precipitation of Cu metal. This consequently stabilizes the high TE performance of polycrystalline Cu_2Se composites under high electric field and large temperature gradient. In addition, the inter-diffusion of Cu vacancies between the Cu_2Se_{1+x} host matrix and BiCuSeO nano phase during the synthesis process efficiently regulates carrier (hole) concentration around the optimal range for a wide series of compositions. Coupled with the enhanced phonon scattering created by the BiCuSeO nano phase, the overall approach solves the dilemma of phase stability and high TE performance.

2. RESULTS AND DISCUSSION

Stoichiometric amounts of Cu, Se, and Bi_2SeO_2 were mixed and reacted into Cu_2Se_{1+x} / yBiCuSeO (x = 0, 0.005, 0.010, 0.015, 0.020; y = 0, 0.05, 0.1, 0.3, 0.5 mol%) composites by self-propagating high-temperature synthesis (SHS) reactions[7, 37-39], and densified by the plasma activated sintering (PAS). There are two basic control parameters in this work: the Se excess amount "x" (a.k.a. Cu vacancy) and the mole fraction "*y*" of BiCuSeO. The relative density of the composite sample is about 95% of the theoretical value, 1~2% lower than that

of the pristine material. The primary phase of all samples at room temperature was confirmed to be α-Cu_2Se[40]. The presence of the BiCuSeO phase was verified by X-ray diffraction (XRD) measurements in samples with a significant content of BiCuSeO (e.g., y = 0.5 mol%) (**Figure S1**), which documented the crucial role of Bi_2SeO_2 in the SHS reaction with Cu and Se to form the BiCuSeO compound[39].

The as-formed Cu_2Se_{1+x} / yBiCuSeO composites exhibit excellent TE properties (**Figures S2 – S19**). Incorporation of BiCuSeO in the Cu_2Se matrix improves the TE properties dramatically. The peak ZT values (ZT_{peak}) of a wide range of composites are above 2 at 973 K (**Figure S2**). Specifically, the ZT_{peak} values of $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO and $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO at 973 K are 2.7 and 2.6, increased by 50% and 44.4%, respectively, compared to $Cu_2Se_{1.005}$ (ZT_{peak}=1.8) and $Cu_2Se_{1.020}$ (ZT_{peak}=1.8) (**Figure 1**(a)). Meanwhile, the average ZT value (ZT_{avg}) of $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO and $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO in the range of 400 K to 973 K is 1.52 and 1.44, increased by 79% and 118%, respectively, compared to $Cu_2Se_{1.005}$ (ZT_{avg}=0.85) and $Cu_2Se_{1.020}$ (ZT_{avg}=0.66).

The repeatability and reproducibility of high ZT values are often an issue. In this work, the electrical conductivity, Seebeck coefficient, thermal conductivity, and calculated ZT curves of the composites are shown to be well repeatable and reproducible (**Figures S9**, **S12**, **S17** and **S18**). In addition, freshly-prepared samples $Cu_2Se_{1.005}$/ 0.1 mol% BiCuSeO and $Cu_2Se_{1.020}$ /

0.3 mol% BiCuSeO were cross-checked at the University of Michigan (UM, ZEM-3 in Prof. P. F. P. Poudeu's laboratory) and Huazhong University of Science and Technology (HUST, LFA427 in Prof. Junyou Yang's laboratory). The results agree well with ours, within the instrumental errors (**Figure 1(a)**, **Figure S19**).

With the excellent TE performance confirmed, an important question pertains to the stability of Cu_2Se. To evaluate the stability of the material, measurements of the conductivity of Cu^+ ions and endurance tests under operational conditions of high current density and large temperature difference were performed. A direct-current polarization method with electron-blocking electrodes was utilized to isolate the ionic conduction by filtering electronic conduction. Solid-state Cu|CuBr|Cu_2Se|CuBr|Cu symmetric pseudo-galvanic cells with the electron blocking CuBr|Cu electrodes were constructed[41, 42] (cf. **Figures S20 - S21**). Upon applying a voltage across the composite, keeping the constant current density of ~ 160 mA/cm^2 (i. e., 100 mA DC passing through the sample), the polarization voltage of the pristine Cu_2Se starts to drop with time, indicating an increased electrical conductivity and thus Cu-precipitation (**Figure 1(b)**). The critical voltage for Cu-precipitation in Cu_2Se is ~ 0.1 - 0.14 V, consistent with the previous report[35]. In sharp contrast, upon incorporating BiCuSeO, the stable polarization voltage increases to above 1.0 V for $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO and to 6.0 V for $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO (**Figure 1(c) and 1(d)**). This indicates that the

incorporation of a small amount of BiCuSeO dramatically improves the stability of the Cu_2Se matrix. In addition, based on the DC polarization measurements, the ionic conductivities of Cu_2Se, $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO, and $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO at 693 K were found to be about 20 Sm^{-1}, 2.2 Sm^{-1} and 0.33 Sm^{-1}, respectively (**Figure 1(b-d)**, **Figure S22**). Evidently, the Cu^+ conductivity in the composites is suppressed by about two orders of magnitude compared to the pristine Cu_2Se, well accounting for their excellent phase stability and reproducibility.

Another evidence of the improved phase stability comes from the shape of a potential variation curve of the pseudo-galvanic cell. Cu precipitation is the result of an electrochemical reaction that alters the shape of the potential variation curve. In the absence of Cu precipitation, the potential is almost constant over polarization time. However, with Cu metal precipitating (phase segregation), a notable potential drop over time is observed at a fixed current[41-43]. Clearly, under a 100 mA, the potential across the pristine Cu_2Se decreases gradually with polarization time, indicating the phase instability with Cu precipitation[41, 43]. With the presence of BiCuSeO, however, the potential across $Cu_2Se_{1.005}$ / 0.1% BiCuSeO and $Cu_2Se_{1.020}$ / 0.3% BiCuSeO samples is not only higher but, more importantly, remains constant upon the same high current of 100 mA. This corroborates the excellent phase stability of the composite under a high current flow.

Moreover, it is well known that the liquid-like nature of Cu^{+} ions in the β-phase of the Cu_2Se structure destabilizes the material under sufficiently large current densities and/or temperature differences. **Figures 1(e-f)** and **S23 - S33** present the morphology and electrical properties of Cu_2Se, $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO, and $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO composites before and after passing a direct current density of 18 Acm^{-2} at 773 K, or applying a 500 K temperature gradient (with the high temperature end at 793 K, and the low temperature end at 293 K).

When the current density of 18 Acm^{-2} was passed through a pristine Cu_2Se sample at 773 K for 3 h, serious pulverization and Cu precipitation occurred, and the electrical properties of the damaged sample could not be characterized (**Figure S25(a)**). Under the DC current density of 18 Acm^{-2} and a temperature difference of 500 K across the sample held for 3 h, massive precipitation of Cu, together with a greatly increased electrical conductivity and decreased Seebeck coefficient (**Figures S30(a), S31**), was observed. This confirms that Cu_2Se is unstable when subjected to large current densities and/or temperature gradients.

The presence of BiCuSeO makes a key difference in the above behavior. For example, the morphology of $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO and $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO samples showed no discernible change after applying 18 Acm^{-2} to the sample for 2 weeks (336 h) at 773 K or imposing a 500 K temperature gradient (**Figure S25(b-c)** and **S30(b-c)**)! Meanwhile,

the electrical conductivity and the Seebeck coefficient measured before and after applying the current and / or the temperature difference returned essentially the same values (**Figures S26**, **S27**, **S32**, and **S33**). Hence, a trace amount of BiCuSeO as a secondary phase dramatically improves the phase stability of the composite.

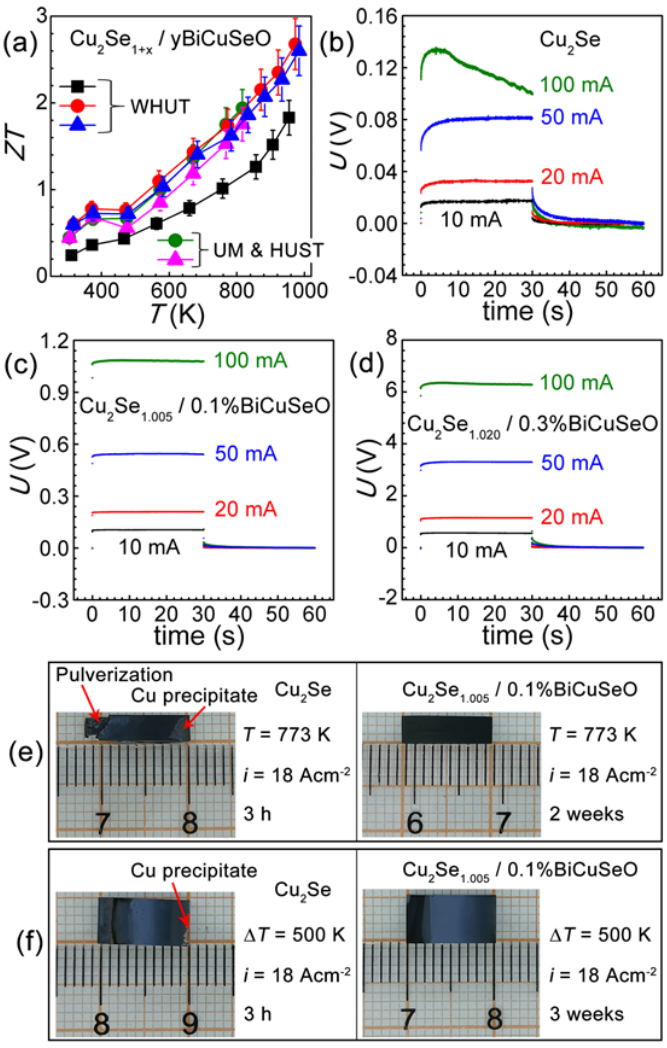

Figure 1 (a) Temperature dependence of the ZT values of Cu_2Se_{1+x} / yBiCuSeO composites. Squares, circles and triangles represent Cu_2Se, $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO, $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO samples, respectively. The black, red and blue ones indicate testing at Wuhan University of Technology (WHUT) and the brown and pink ones designate cross checking at the University of Michigan (UM, ZEM-3 in Prof. P. F. P. Poudeu's laboratory) and Huazhong University of Science and Technology (HUST, LFA427 in Prof. Junyou Yang's laboratory). Potential variation curves for Cu_2Se (b), $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO (c), $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO (d) under different test current at 693 K applied for 30 sec. The resulting ionic conductivities at 693 K of Cu_2Se, $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO, $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO were found to be ~ 20 Sm^{-1}, 2.2 Sm^{-1} and 0.33 Sm^{-1}, respectively. (e) Comparison between Cu_2Se and $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO when a current of 18 Acm^{-2} was passed through at 773 K, (f) Comparison between Cu_2Se and $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO while passing a current of 18 Acm^{-2} through the samples as well as applying a 500 K temperature gradient (T-hot ~ 793 K, and T-cold ~ 293 K).

How can such a small amount of well dispersed BiCuSeO nanoparticles be so effective in preventing the migration of Cu^+ ions? In order to reveal the underlying mechanism for this

surprising phenomenon, we studied the microstructure and Cu_2Se/BiCuSeO interface in details from different aspects.

Figures 2(a) - 2(b) show HAADF-STEM images at low magnification and corresponding elemental map (Bi/Cu) of the $Cu_2Se_{1.005}$ / 0.1mol%BiCuSeO bulk material. Apparently, a large number of uniformly distributed pores with sizes ranging from tens of nanometer to several hundred nanometers are observed. The edge of the pores is rich in Bi, indicating BiCuSeO is mainly attached on their inner wall. Such morphology is strongly related to the formation process of BiCuSeO and is common among mesoporous materials prepared by sacrificial template methods[44]. In an early work, we have demonstrated the crucial role of Bi_2SeO_2 (**Figure S34**) in the SHS reaction with Cu, and Se to form the nanosized crystals of BiCuSeO (**Figure S35 - S36**)[39] with a polygonal lamellar morphology (**Figure S37**). It should be mentioned that no Cu metal precipitate was found inside the nano pores of the Cu_2Se_{1+x} / yBiCuSeO composites before or after the stability measurements under a high current flow or a temperature gradient. Therefore, the uniform distribution of BiCuSeO nanocrystals within the Cu_2Se matrix forms a large number of interfaces which effectively block Cu-ion diffusion. **Figure 2(c)** shows the HR-STEM image of the interface between Cu_2Se and BiCuSeO in $Cu_2Se_{1.005}$ / 0.1mol%BiCuSeO bulk material around the pore. The electron diffraction for Cu_2Se and BiCuSeO indicates that BiCuSeO epitaxially grows on the (1 3 1) plane of Cu_2Se

coherently where [3 -1 0] zone axis of Cu_2Se crystal being parallel with [2 2 -1] zone axis of BiCuSeO crystal. As a result, the (0 0 2) and (1 3 1) planes of Cu_2Se are nearly parallel with (1 0 2) and (0 -1 2) planes of BiCuSeO, respectively. This kind of interface would facilitate the formation of Cu^+ modulated electric double layer between Cu_2Se and BiCuSeO, which plays a key role for stabilizing Cu_2Se.

It is well known that both Cu^+ ion and hole carriers in Cu_2Se participant in the electric transport. Thus, understanding the role of Cu^+ ions and the charge transfer at the Cu_2Se/BiCuSeO interface is the key to revealing the underlying mechanism for the enhanced stability. In order to shed light on the charge transfer at the Cu_2Se/BiCuSeO heterojunction, the ultraviolet photoemission spectroscopy (UPS) spectra of Cu_2Se and BiCuSeO compounds were collected, shown in **Figure 2(d)** and **2(e)**, respectively. The work function of Cu_2Se and BiCuSeO are 5.16 eV and 5.52 eV, respectively. The difference in the work function would drive the hole transfer from BiCuSeO to Cu_2Se, concomitantly forming a depletion layer with the raw built-in electric field in the Cu_2Se/BiCuSeO heterojunction pointing from Cu_2Se to BiCuSeO (**Figure 2(f)**). This raw built-in electric field in the Schottky heterojunction is also confirmed by a nonlinear feature in *I-U* curve (**Figure 2(g)**) in comparison with linearly symmetric *I-U* curve of pristine Cu_2Se and pristine BiCuSeO (**Figure S39**). This impacts the charge transfer between Cu_2Se and BiCuSeO.

In order to probe the behavior of charge carrier and Cu^+ ions at the heterojunction, forward scan and backward scan of *I-U* curves were measured with the input voltage in the range from -3.5 V to 3.5 V. Clearly, under the forward scan the current is smaller than that under the reverse scan, regardless of the current directions, resulting in a hysteretic behavior in the *I-U* curve (**Figure 2(g)**). It is well known that the capacitive effect as the Schottky heterojunction can act as a capacitor accumulating charges or Cu^+ ions at the interface due to the potential difference. However, in the case of the electron capacitor, the current under forward scan should be larger than that under the backward scan, which is opposite to experimental observation in the Cu_2Se/BiCuSeO heterojunction. Therefore, the hysteretic gap in the *I-U* curve of the Cu_2Se/BiCuSeO heterojunction is predominantly ascribed to capacitive effects of Cu^+ ions at the interface. The slow reconfiguration process of Cu^+ ion migration is responsible for the hysteresis in the *I-U* curve when the applied voltage is changed. The highly resistive BiCuSeO to the passage of Cu^+ ions, the potential difference between Cu_2Se and BiCuSeO, and the unilateral conductivity of the Schottky junction allow accumulation of mobile Cu^+ ions at the Cu_2Se / BiCuSeO interfaces under the current flowing from Cu_2Se to BiCuSeO. In addition, it is worth noting that due to the unilateral conductivity of the Schottky junction, positive bias voltage allows accumulation of Cu^+ ions at the interface, while the negative bias voltage expels Cu^+ ions from the interface and they migrate and redistribute along the current direction in the host matrix. The difference in the Cu^+ ions concentration in the two sides of

the interface region modifies the potential barrier for injection of electronic carrier, leading to the abnormal asymmetry in the *I-U* curve of the Cu_2Se/BiCuSeO heterojunction, which is distinguished from an ideal Schottky junction.

This accumulation of Cu^+ ions at the interface under the direct current induces interfacial electronic dipole polarization, forming a negatively charged surface on BiCuSeO as sketched in **Figure 2(h)**. This is accompanied with the formation of an electric double charge layer and an electrostatic field. The formed space charge region in the Cu_2Se and BiCuSeO nano-particle, where BiCuSeO nano-particle is equivalent to a positive point charge due to the capacitive effects of Cu^+ ions, further impedes migration of Cu^+. This agrees well with the much lower Cu^+ conductivity (0.33 S/m *vs*. 20 S/m for Cu_2Se) and higher critical voltage (> 1 V *vs*. 0.13 V for Cu_2Se) observed in the Cu_2Se_{1+x} / yBiCuSeO nanocomposites. Furthermore, the increase of external voltage difference between Cu_2Se matrix and BiCuSeO nano-particle, drives more Cu^+ ions to accumulate at the interface, thereby reinforcing the electrostatic field formed in the space charge region. Thus, in spite of the small volume fraction of BiCuSeO, the Coulomb force around the BiCuSeO nanoparticles effectively blocks long-range motion of Cu^+ through the sample.

Along with the highly mobile Cu^+ ions, Cu metal precipitation at the surface and interface is also a major problem for the stability of Cu_2Se. Practically, Cu metal precipitation is an

electrochemical reduction reaction process where the highly mobile Cu^+ ions at the interface or surface close to the upper limit concentration accept electron from the matrix, forming Cu metal[35]. Although the aforementioned Schottky Cu_2Se/BiCuSeO heterojunction facilitates the accumulation of a higher concentration of Cu^+ ions at the interface over that inside of the matrix, the potential difference in the Schottky junction impedes the electron transfer from BiCuSeO to Cu_2Se, unless the energy of electrons is high enough to overcome the potential difference (**Figure 2(i)**). Therefore, this special heterojunction obstructs the reduction reaction the Cu^+ ions accumulated at the interface. Thus, incorporation of BiCuSeO not only blocks the long-range migration of Cu^+ ions throughout the sample but it also imposes a potential barrier for the reduction of Cu^+ ion into Cu metal. All these effects contribute to the stabilized Cu-ions in the composite.

To gain more insights into the microscopic nature of ionic migration between Cu_2Se and BiCuSeO, we conducted an *in situ* transmission electron microscopy study. **Figure S40** shows a HAADF image and EDS mapping results for the Cu_2Se/BiCuSeO heterojunction. As identified by the high resolution image and its corresponding diffraction pattern (**Figure S40**), the crystal on the left of the heterojunction is Cu_2Se, while the one on the right is BiCuSeO. When the current flows from BiCuSeO to Cu_2Se (corresponding to the formation of Cu aggregates at the contact point), the critical voltage (threshold) for deposition of Cu metal is

1.1 V (**Figure 3(a)**). However, when the current flows in the opposite direction from Cu_2Se to BiCuSeO (corresponding to the disappearance of Cu aggregates at the contact point), the critical voltage for rapid Cu^+ migration is 2.3 V (**Figure 3(b)**). Moreover, no Cu deposition is observed at the Cu_2Se/BiCuSeO interface despite the fact that the applied reverse voltage is much higher than the forward voltage. Obviously, when the current flows from Cu_2Se to BiCuSeO, the electrostatic field formed by the accumulated Cu^+ ions will oppose migration of Cu^+ from the Cu_2Se matrix and the Schottky heterojunction of Cu_2Se/BiCuSeO increases the potential barrier for electron transfer from BiCuSeO to Cu_2Se. Hence, the critical voltage for rapid migration of Cu^+ ions is significantly increased and no Cu deposition is detected. This further corroborates the Cu^+ ion blocking mechanism in Cu_2Se_{1+x} / yBiCuSeO composites and the presence of an additional electrostatic field under the current.

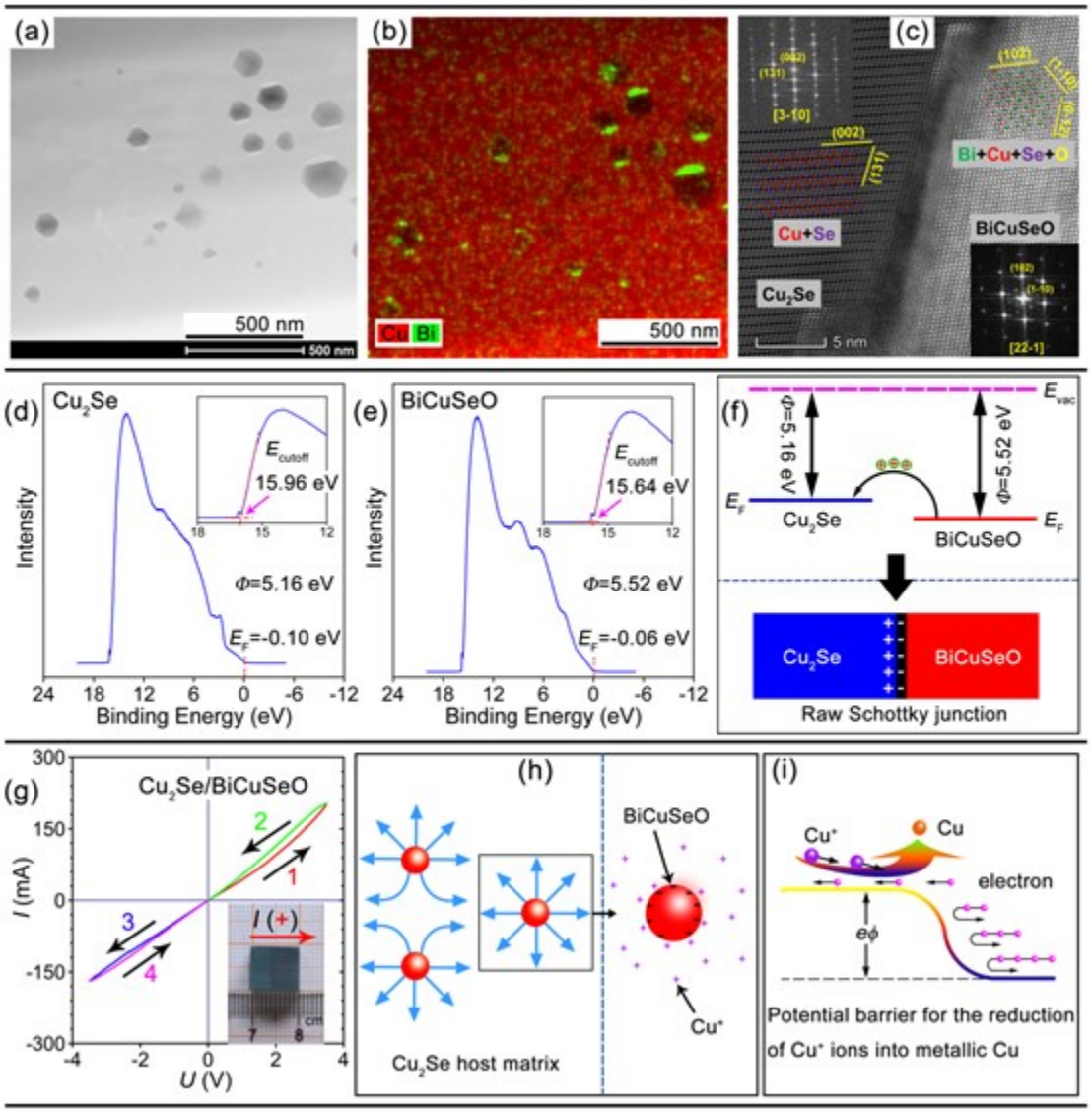

Figure 2. (a) HAADF-STEM image at low magnification of $Cu_2Se_{1.005}$ / 0.1mol%BiCuSeO bulk material, the pores are dark. (b) EDS color elemental map (Bi/Cu) of the whole area in (a). (c) Interface between Cu_2Se and BiCuSeO around the pore. Orientation relationship: Cu_2Se [3 -1 0] // BiCuSeO [2 2- 1], Cu_2Se (0 0 2) // BiCuSeO (1 0 2), Cu_2Se (1 3 1) // BiCuSeO (0 -1 2). (d)

and (e) Ultraviolet photoemission spectrum (UPS) of the Cu_2Se and BiCuSeO. the Fermi edge (E_F) is identified in the diagram, and the secondary electron cutoff edge (E_{cutoff}) is highlighted in the illustration. (f) A schematic diagram of hole transfer from BiCuSeO to Cu_2Se driven by the difference in their work functions, and the formation of Cu_2Se-BiCuSeO heterojunction, with the direction of the initial built-in electric field pointing from Cu_2Se to BiCuSeO. (g) I-U curve of a Cu_2Se/BiCuSeO heterojunction. Clearly, a nonlinear I-U curve and hysteresis are observed. (h) Schematic illustration of the long range electrostatic field formation and the space charge distribution in electric double layer around BiCuSeO in the Cu_2Se_{1+x} / yBiCuSeO composites. A small amount of Cu^+ ions accumulate at the interface between Cu_2Se_{1+x} matrix and BiCuSeO under an external current. This induces interfacial electronic dipole polarization, leading to negatively charged BiCuSeO surfaces. The formed space charge region in the Cu_2Se and BiCuSeO nanoparticle, where the BiCuSeO nanoparticle is equivalent to a positive point charge due to the capacitive effects of Cu^+ ions. Thus, in spite of a small volume fraction of BiCuSeO, the long-range Coulomb force around BiCuSeO nanoparticles effectively blocks motion of Cu^+ through the sample. (i) A schematic diagram of potential barrier in the Schottky heterojunction, which obstructs the reduction reaction from Cu^+ into Cu metal.

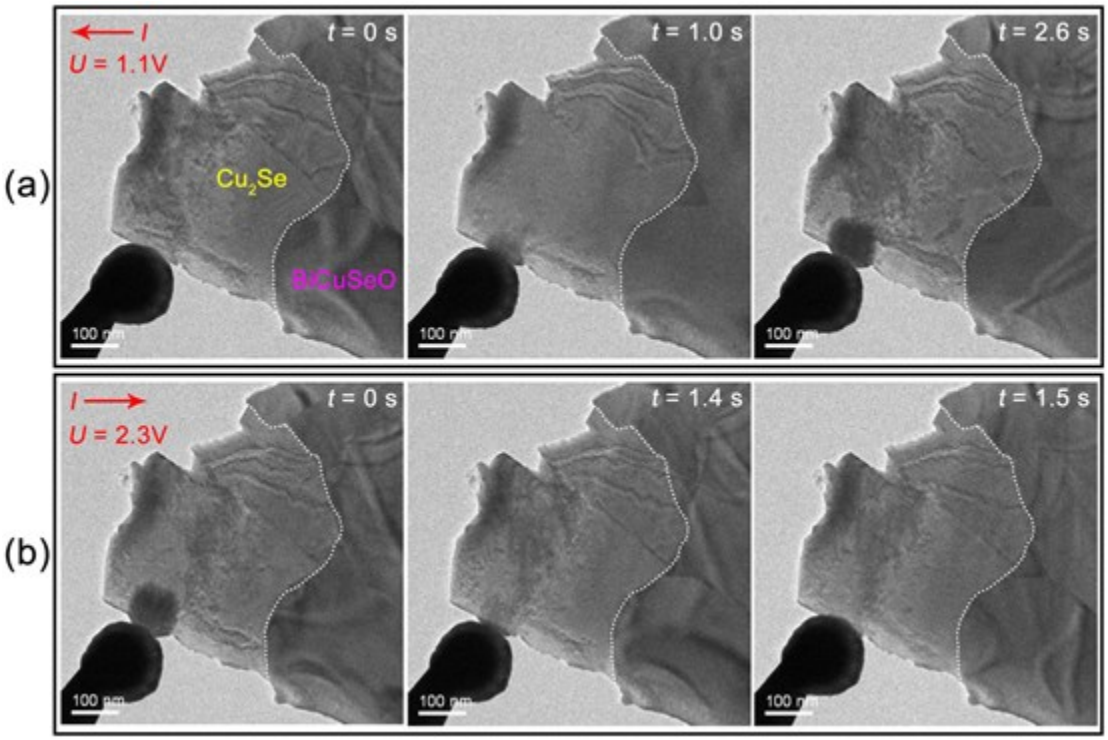

Figure 3 In situ transmission electron microscopy images, (a) Different stages (in time) during the current flow from BiCuSeO to Cu_2Se. The developing black spot in the vicinity of the contact is the precipitated copper, which is observed when the applied voltage reaches the critical value of 1.1 V. (b) Different stages following the current reversal (the current now flows from Cu_2Se to BiCuSeO). In this case, the critical voltage for rapid migration of Cu^+ (i.e., the disappearance of the previously precipitated copper) is 2.3 V.

Obviously, the Cu^+ modulated electric double layer in the space charge region between the Cu_2Se and BiCuSeO phases blocks the long-range ion migration in the entire sample. Along

with the Schottky junction, which prevents electron transfer from BiCuSeO to Cu_2Se and thus hinders the reduction reaction, the high TE performance of the Cu_2Se/BiCuSeO composites is stabilized. Additionally, the TE performance of Cu_2Se / BiCuSeO composites is strongly related to its carrier concentration that is determined by the Cu content, i.e., Cu vacancies in the Cu_2Se host. We now discuss the mechanism for modulation of the carrier concentration. The regulating behavior of the Cu/Se content in the host matrix is confirmed by DSC tests performed on the as-prepared composites (**Figure 4(a) and Figure S41**). For Cu_2Se_{1+x}, the phase transition temperature (T_{tr}) decreases from 399.2 K to 387.4 K as the content of Se increases. For Cu_2Se / yBiCuSeO, $Cu_2Se_{1.005}$ / yBiCuSeO, and $Cu_2Se_{1.010}$ / yBiCuSeO, the T_{tr} tends to shift to a lower temperature, indicating the decreased Cu/Se ratio in the matrix according to the binary Cu-Se phase diagram[45]. For $Cu_2Se_{1.015}$ / yBiCuSeO and $Cu_2Se_{1.020}$ / yBiCuSeO, T_{tr} tends to shift to a higher temperature, implying an increased Cu/Se ratio in the matrix. The DSC results indicate that the presence of Cu^+ vacancies inter-diffusion process during the preparation of Cu_2Se/BiCuSeO composite can modulate the copper content in the host matrix. This helps to maintain the carrier concentration at the optimal region over a wide range of compositions, which is very important for the reproducible synthesis of materials on a large scale.

To reveal and substantiate the mechanism underlying the high TE performance of these composites, low temperature and high temperature transport properties were studied (**Figures S4**, **S6**, **S8**, **S11**, **S14**, **S16, S42 and S43**). Specifically, **Figure 4(b)** shows the relation between the carrier concentration and the composition (x, y) at 600 K. As shown, the optimal carrier concentrations are in the range of 1.0 - 1.5 × 10^{21} cm^{-3}, which yields peak *ZT* values exceeding 2.0. To more clearly see the self-regulation of the carrier concentration by BiCuSeO and Se excess, we present a baseline (red dotted line) derived by assuming that each excess Se atom donates two holes to the composite. Apparently, the presence of BiCuSeO tends to increase (decrease) the carrier concentration when $x \leq 0.01$ (when $x > 0.01$). Since the carrier concentration is positively related to the x-value, the presence of BiCuSeO thus self-regulates the carrier concentration. The pivotal (balance) point is near x = 0.01, where the carrier concentration is around 1.0 × 10^{21} cm^{-3}, close to the lower end of the optimal carrier concentration. It remains an open question how this optimized carrier concentration is achieved over such a wide range of compositions and how it is coordinated with the effectively regulating behavior of Cu vacancies between Cu_2Se and BiCuSeO during the preparation process.

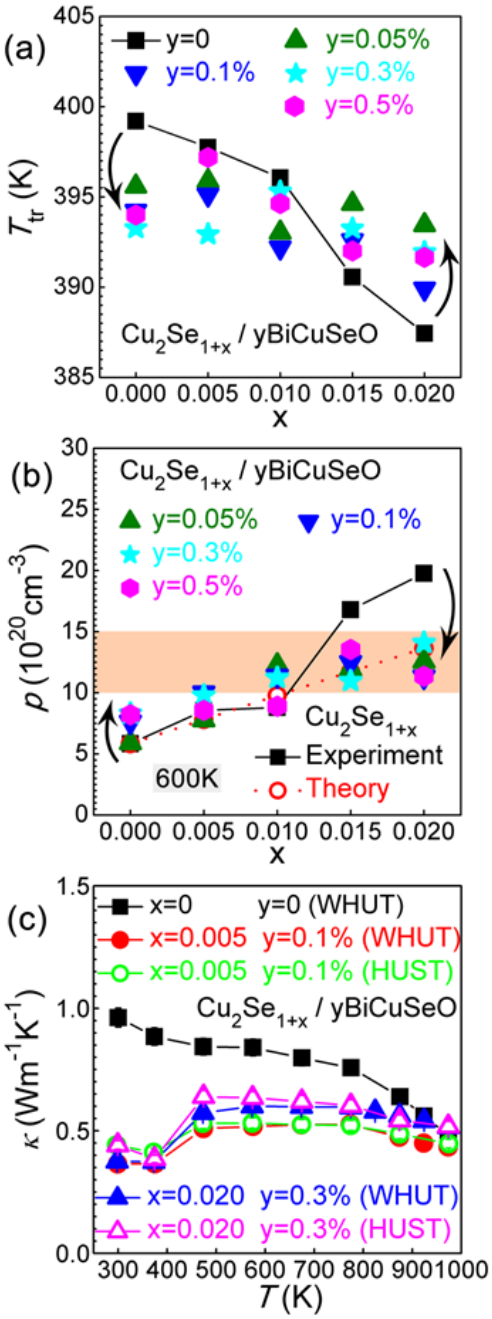

Figure 4 (a) Relationship between the phase transition temperature and composition of composite structures. (b) Relationship between the carrier concentration (p) of holes and

composition of composite structures. The orange region corresponds to the optimal carrier concentration, which yields ZT values exceeding 2.0. Clearly, the incorporation of BiCuSeO can adjust the relative content of copper in the Cu_2Se matrix (as seen in the variation of the phase transition temperature), which, in turn, adjusts the carrier concentration to optimal in a wide range of compositions. (c) Temperature dependence of the total thermal conductivity (k) of Cu_2Se_{1+x} / yBiCuSeO composites. Squares, circles and triangles represent Cu_2Se, $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO, $Cu_2Se_{1.020}$ / 0.3 mol% BiCuSeO samples, respectively. The solid symbols indicate testing at the Wuhan University of Technology (WHUT) while the open symbols designate cross checking at Huazhong University of Science and Technology (HUST, LFA427 in Prof. Junyou Yang's laboratory)

The origin of charge carriers (holes) in Cu_2Se and BiCuSeO is Cu vacancies[4, 46]. Actually, the carrier concentration of Cu_2Se is about 4×10^{20} cm^{-3} due to the Cu vacancies and that of BiCuSeO is about 2×10^{17} cm^{-3} at room temperature[4, 7, 39]. Therefore, driven by the Cu vacancy potential difference, Cu vacancies naturally diffuses from BiCuSeO to Cu_2Se in the Cu_2Se_{1+x} / yBiCuSeO composite when $x \leq 0.01$, and then diffuses from Cu_2Se to BiCuSeO when $x \geq 0.01$. This points to the effective regulation of the relative copper content in the host matrix.

The remarkable reduction of the already low thermal conductivity of Cu_2Se in the composite samples is a contributing factor to the high TE performance. As noticed, the Cu_2Se_{1+x} / yBiCuSeO nanocomposites exhibits low thermal conductivity (**Figure 4(c)**), especially at some particular compositions, *e.g.* $Cu_2Se_{1.005}$ / 0.1 mol% BiCuSeO (**Figure S7**), $Cu_2Se_{1.010}$ / 0.3 mol% BiCuSeO (**Figure S10**), $Cu_2Se_{1.015}$ / 0.1 mol% BiCuSeO (**Figure S13**), $Cu_2Se_{1.020}$ / 0.1 mol% BiCuSeO, and $Cu_2Se_{1.02}$ / 0.3 mol% BiCuSeO (**Figure S15**). It should be noted that the low thermal conductivity was crosschecked by other group (HUST).

The exact origin of the ultra-low thermal conductivity in Cu_2Se, however, has been the subject of debate. Several different theories have been proposed. For example, some investigations show that the liquid-like diffusion of Cu^+ ions suppresses the transverse phonons, leading to a dramatically reduced thermal conductivity. They conclude that the higher the ionic conductivity, the lower the thermal conductivity. In contrast, other investigations show that migration of Cu^+ ions cannot prevent the propagation of transverse acoustical phonons, and argue that the lattice anharmonicity, correlated with the diffusion of Cu^+ (diffusion rate and hopping time), is the main origin of the low thermal conductivity[47]. In the context of our experimental data, the decrease in the ionic migration in the samples upon incorporating BiCuSeO nano-particles is unequivocal. This modified process of dynamic Cu^+ ions may intensify phonon scattering, suppressing the lattice thermal conductivity[47, 48]. Moreover,

BiCuSeO nanoparticles and nano pores enhance interfacial phonon scattering and strongly scatter the heat-carrying phonons, resulting in an additional reduction of the thermal conductivity and thus high *ZT* in Cu_2Se_{1+x} / yBiCuSeO composites.

3. CONCLUDING REMARKS

Through an *in situ* incorporation of nanoparticles of BiCuSeO, the superionic nature of Cu_2Se in macroscopic samples was largely eliminated while maintaining excellent TE properties. The superior phase and physical property stability is realized by creating an ion-modulated interfacial electrostatic field under the direct current that blocks the long-range migration of Cu^+ ions across Cu_2Se_{1+x} / BiCuSeO interfaces and prevents the reduction reaction from Cu^+ to Cu metal. Meanwhile, the effective regulation of the relative content of copper and the concentration of holes in the host matrix through inter-diffusion of Cu vacancies between the Cu_2Se_{1+x} host matrix and the BiCuSeO nanophase during the synthesis process maintains high power factor and the carrier concentration at the optimal carrier concentration range over a wide temperature and composition region. These effects stabilize the excellent TE performance under high current/voltage and/or large temperature gradient. Moreover, the lattice phonons are strongly scattered by BiCuSeO nanoparticles and nano pores, dramatically reducing the lattice thermal conductivity. Owing to the optimal hole concentration

and the dramatically suppressed thermal conductivity, the Cu_2Se_{1+x} / yBiCuSeO composites attain high peak *ZT*s of ~ 2.7 at 973 K, and the corresponding average *ZT* values between 400 K and 973 K reach a high value of 1.5. The excellent repeatability and reproducibility of TE properties strongly substantiate the proposed mechanism. The results highlight a new strategy for the active control of ion migration and may have broader implications for the stabilization of other systems such as halide perovskites and solid state interfacial behavior in solid state batteries and fuel cells.

ASSOCIATED CONTENT

Supporting information

Synthesis of Cu_2Se_{1+x} / yBiCuSeO composites

Figures S1 - S43

3D reconstruction for a pit of $Cu_2Se_{1.005}$ / 0.1%BiCuSeO composite

In situ transmission electron microscopy.

The supporting information is available free of charge from the internet or from the authors.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

1. D. M. Rowe, *CRC Handbook of Thermoelectrics*, CRC Press, Boca Raton, 1995.
2. H. J. Goldsmid, *Introduction to Thermoelectricity*, Springer, 2010.
3. J. He and T. M. Tritt, *Science*, 2017, 357, 1369.

4. H. L. Liu, X. Shi, F. F. Xu, L. L. Zhang, W. Q. Zhang, L. D. Chen, Q. Li, C. Uher, T. Day and G. J. Snyder, *Nat Mater*, 2012, 11, 422.

5. R. Nunna, P. F. Qiu, M. J. Yin, H. Y. Chen and L. D. Chen, *Energy Environ. Sci.,* 2017, **10**, 1928.

6. A. A. Olvera, N. A. Moroz, P. Sahoo, P. Ren, T. P. Bailey, A. A. Page, C. Uher and P. F. P. Poudeu, *Energy Environ. Sci.,* 2017, 10, 1668.

7. X. L. Su, F. Fu, Y. G. Yan, G. Zheng, T. Liang, Q. Zhang, X. Cheng, D. W. Yang, H. Chi, X. F. Tang, Q. J. Zhang and C. Uher, *Nat Commun*, 2014, 5, 4908.

8. Y. He, T. Day, T. S. Zhang, H. L. Liu, X. Shi, L. D. Chen and G. J. Snyder, *Adv. Mater.,* 2014, 26, 3974.

9. Y. He, P. Lu, X. Shi, F. F. Xu, T. S. Zhang, G. J. Snyder, C. Uher and L. D. Chen, *Adv. Mater.*, 2015, 27, 3639.

10. X. X. Xiao, W. J. Xie, X. F. Tang and Q. J. Zhang, *Chinese Phys. B,* 2011, **20**, 340.

11. G. J. Snyder, M. Christensen, E. Nishibori, T. Caillat and B. B. Iversen, *Nat. Mater.,* 2004, **3**, 458.

12. T. Caillat, J. P. Fleurial and A. Borshchevsky, *J. Phys. Chem. Solids,* 1997, **58**, 1119.

13. M. Ferhat and J. Nagao, *J. Appl. Phys.,* 2000, **88**, 813.

14. Y. F. Ding, Y. Qiu, K. F. Cai, Q. Yao, S. Chen, L. D. Chen and J. Q. He, *Nat. Commun.,*2019, **10**, 841.

15. Y. Z. Pei, N. A. Heinz and G. J. Snyder, *J. Mater. Chem.,* 2011, **21**, 18256.

16. D. W. Yang, X. L. Su, F. C. Meng, S. Wang, Y. G. Yan, J. H. Yang, J. He, Q. J. Zhang, C. Uher, M. G. Kanatzidis and X. F. Tang, *J. Mater. Chem. A,* 2017, **5**, 23243.

17. X. Shi, H. Y. Chen, F. Hao, R. H. Liu, T. Wang, P. F. Qiu, U. Burkhardt, Y. Grin and L. Chen, *Nat. Mater.,*2018, **17**, 421.

18. B. Li, H. Wang, Y. Kawakita, Q. Zhang, M. Feygenson, H. L. Yu, D. Wu, K. Ohara, T. Kikuchi, K. Shibata, T. Yamada, X. K. Ning, Y. Chen, J. Q. He, D. Vaknin, R. Q. Wu, K. J. Nakajima and M. G. Kanatzidis, *Nat. Mater.,* 2018, **17**, 226.

19. J. L. Niedziela, D. Bansal, A. F. May, J. X. Ding, T. Lanigan-Atkins, G. Ehlers, D. L. Abernathy, A. Said and O. Delaire, *Nat. Phys.,* 2019, **15**, 73.

20. W. Li, S. Q. Lin, B. H. Ge, J. Yang, W. Q. Zhang and Y. Z. Pei, *Adv. Sci.,* 2016, **3**, 1600196.

21. W. F. Kuhs, R. Nitsche and K. Scheunemann, *Mater. Res. Bull.,* 1979, **14**, 241.

22. X. Shen, C. C. Yang, Y. M. Liu, G. W. Wang, H. Tan, Y. H. Tung, G. Y. Wang, X. Lu, J. He and X. Y. Zhou, *ACS Appl. Mater.Inter.,*2018, **11**, 2168.

23. W. Li, S. Q. Lin, M. Weiss, Z. W. Chen, J. Li, Y. D. Xu, W. G. Zeier and Y. Z. Pei, *Adv. Energy Mater.,* 2018, **8**, 1800030.

24. S. Q. Lin, W. Li, S. Li, X. Zhang, Z. Chen, Y. Xu, Y. Chen and Y. Pei, *Joule*, 2017, 1, 816.

25. B. Jiang, P. Qiu, H. Chen, Q. Zhang, K. Zhao, D. Ren, X. Shi and L. Chen, *Chemical Communications*, 2017, 53, 11658.

26. T. P. Bailey and C. Uher, *Current Opinion in Green and Sustainable Chemistry,* 2017, **4**, 58.

27. E. F. Hampl Jr, Minnesota Mining and Mfg. Co., St. Paul (USA). Technical Ceramic Products Div., 1976.

28. N. B. Elsner and J. Chin, General Atomic Co., San Diego, Calif. (USA), 1975.

29. C. J. Goebel and T. E. Hammel, Teledyne Co., Program final report (NO. TES-33009-46), 1978.

30. G. Stapfer and V. C. Truscello, Report NO. 19770066000, NASA JPL, 1977.

31. G. Stapfer, Jet Propulsion Lab., Pasadena, CA (USA), 1977.

32. T. P. Bailey, H. Si, H. Y. Xie, A. Olvera, P. F. P. Poudeu, X. F. Tang and C. Uher, *J. Mater. Chem. A*, 2016, **4**, 17225.

33. G. Dennler, R. Chmielowski, S. Jacob, F. Capet, P. Roussel, S. Zastrow, K. Nielsch, I. Opahle and G. K. H. Madsen, *Adv. Energy Mater.,* 2014, **4**, 1301581.

34. D. R. Brown, T. Day, T. Caillat and G. J. Snyder, *J. Electron. Mater.,* 2013, **42**, 2014.

35. P. F. Qiu, M. T. Agne, Y. Y. Liu, Y. Q. Zhu, H. Y. Chen, T. Mao, J. Yang, W. Q. Zhang, S. M. Haile, W. G. Zeier, J. Janek, C. Uher, X. Shi, L. D. Chen, G. J. Snyder, *Nat. Commun.,* 2018, **9**, 2910.

36. P. F. Qiu, T. Mao, Z. F. Huang, X. G. Xia, J. C. Liao, M. T. Agne, M. Gu, Q. H. Zhang, D. D. Ren, S. Q. Bai, X. Shi, G. J. Snyder and L. D. Chen, *Joule,* 2019, 3, 1.

37. A. G. Merzhanov, *Arch. Combustionis*, 1981, 1, 23.

38. A. G. Merzhanov, *Combust. Sci. Technol.,* 1994, **98**, 307.

39. D. W. Yang, X. L. Su, Y. G. Yan, T. Z. Hu, H. Y. Xie, J. He, C. Uher, M. G. Kanatzidis and X. F. Tang, *Chem. Mater.,* 2016, **28**, 4628.

40. W. J. Qiu, P. Lu, X. Yuan, F. F. Xu, L. H. Wu, X. Z. Ke, H. L. Liu, J. Yang, X. Shi, L. D. Chen, J. H. Yang, W. Q. Zhnag, *J. Chem. Phys.,* 2016, **144**, 194502.

41. I. Yokota, *J Phys. Soc. Jpn.,* 1953, **8**, 595.

42. I. Yokota, *J. Phys. Soc. Jpn.,* 1961, **16**, 2213.

43. Y. Y. Liu, P. F. Qiu, H. Y. Chen, R. Chen, X. Shi and L. D. Chen, *J. Inorg. Mater.,* 2017, **32**, 1337.

44. M. Oschatz, J. T. Lee, H. Kim, W. Nickel, L. Borchardt, W. I. Cho, C. Ziegler, S. Kaskel and G. Yushin, *J. Mater. Chem.,* 2014, *A* **2**, 17649.

45. V. M. Glazov, A. S. Pashinkin and V. A. Fedorov, *Inorg. Mater.,* 2000, **36**, 641.

46. L. D. Zhao, J. Q. He, D. Berardan, Y. H. Lin, J. F. Li, C. W. Nan and N. Dragoe, *Energy Environ. Sci.,* 2014, **7**, 2900.

47. D. J. Voneshen, H. C. Walker, K. Refson and J. P. Goff, *Phys. Rev. Lett.,* 2017, **118**, 145901.

48. X. Liang, *Appl. Phys. Lett.*, 2017, 111, 133902.

The space charge region between the Cu_2Se host matrix and *in situ* formed BiCuSeO under a direct current causes drastic suppression of Cu^+ ion migration in the composites, and obstructs the reduction reaction of Cu^+ into Cu metal, which, together with the effective regulation of carrier concentration as well as enhanced interfacial phonon scattering, greatly stabilizes the improved thermoelectric performance.