



Cite this: *J. Mater. Chem. A*, 2022, 10, 19829

## Unusual thermoelectric properties mediated by solute segregation in tellurium alloyed CoSbS†

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The doping or alloying effect is effective for tuning the carrier concentration and/or lowering the lattice thermal conductivity in thermoelectrics. Herein, taking  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{1-x}\text{Te}_x$  as a typical example, we observed an unusual phenomenon where Te alloying mediates grain growth. It was observed that the Te dopant tended to be segregated along grain boundaries as a precipitate, resulting in an increase in grain size from 0.36  $\mu\text{m}$  to 0.57  $\mu\text{m}$ . The grain growth optimizes the low-temperature carrier scattering mechanism, leading to a higher power factor that represents a superior value in advanced sulfur-based thermoelectric materials. The lattice thermal conductivity was, however, slightly suppressed, which was higher than the Debye-model prediction. As a compromise, the average thermoelectric figure of merit ( $zT$ ) was enhanced after Te doping, higher than those of other CoSbS based materials. Overall, this work proves the significance of solute segregation in the optimization of thermoelectric performance.

Received 18th March 2022  
Accepted 13th May 2022

DOI: 10.1039/d2ta02147a

rsc.li/materials-a

### Introduction

Thermoelectric devices can directly convert a temperature gradient to electricity and *vice versa*, which plays a vital role in

the applications of these materials in aerospace power, refrigeration, and energy harvesting.<sup>1–3</sup> The corresponding thermoelectric performance, including the conversion efficiency for power generation and the cooling coefficient of performance for cooling applications, is dominated by the dimensionless thermoelectric figure of merit ( $zT$ ), which is defined as  $zT = (S^2\sigma/\kappa_{\text{tot}})T$ , where  $S$ ,  $\sigma$ ,  $\kappa_{\text{tot}}$ , and  $T$  are the Seebeck coefficient, electrical conductivity, total thermal conductivity (including lattice thermal conductivity  $\kappa_{\text{lat}}$  and electronic thermal conductivity  $\kappa_{\text{ele}}$ ), and absolute temperature, respectively.<sup>4</sup> To enhance the  $zT$  of a target material, conventional strategies rely on carrier concentration optimization to increase the power factor ( $\text{PF} = S^2\sigma$ ) and/or isoelectronic alloying to strengthen phonon scattering to suppress  $\kappa_{\text{lat}}$ .<sup>5–8</sup>

Over the last two decades, the significance of microstructural engineering in tuning thermoelectric properties was realized and demonstrated,<sup>9</sup> in which a remarkable effect was demonstrated where  $\kappa_{\text{lat}}$  was reduced through delicate control of the material synthesis process to introduce phonon-scattering centers, *e.g.*, grain boundaries,<sup>10–13</sup> nanoprecipitates,<sup>14,15</sup> dislocations,<sup>16–18</sup> and pores.<sup>19,20</sup> In contrast, few relevant studies have focused on the influence of microstructural defects on carrier transport. Very recently, it was found that grain boundary scattering, a previously overlooked factor, plays a vital role in the carrier scattering strength for some thermoelectric material systems, *e.g.*,  $\text{Mg}_2\text{Si}$ ,<sup>21</sup>  $\text{Mg}_3\text{Sb}_2$ ,<sup>22–24</sup>  $\text{PbSe-NaSbSe}_2$ ,<sup>25</sup> and  $\text{Hf}$ /



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† Electronic Supplementary Information (ESI) available. See <https://doi.org/10.1039/d2ta02147a>

ZrCoSb.<sup>26</sup> Eliminating the additional scattering mechanism *via* increasing the grain size is therefore responsible for the experimental maximization of the PF.

Tellurium (Te) based thermoelectric materials, such as low-temperature Bi<sub>2</sub>Te<sub>3</sub>,<sup>10,27–29</sup> and intermediate-temperature PbTe and GeTe,<sup>30–36</sup> exhibit high *zT* values in their working temperature range. However, the scarcity of Te, with an abundance in the Earth's crust of around 0.001 ppm, may restrict their wide applications. Considering the significantly high earth abundance of sulfur (S) of around 350 ppm, S-based materials, including Bi<sub>2</sub>S<sub>3</sub>,<sup>37,38</sup> PbS,<sup>39,40</sup> Cu<sub>2</sub>S,<sup>41,42</sup> and CuFeS<sub>2</sub>,<sup>43,44</sup> have received intensive interest for the replacement of their Te-based counterparts. Due to their increased ionic bonding strength, S-based materials for thermoelectric applications are prone to exhibiting both low  $\sigma$  and PF as a consequence of low charge carrier mobility,  $\mu_{\text{H}}$ . Parker *et al.* first reported the potential thermoelectric performance of a paracostibite CoSbS compound using combined theoretical and experimental analysis.<sup>45</sup> Very recently, this system was demonstrated to have an ultrahigh PF that exceeds the benchmark of 20  $\mu\text{W cm}^{-1} \text{K}^{-2}$  using Ni or Te doping as strong n-type dopants.<sup>46–48</sup> This attractive property is due to the several conduction bands around the Fermi level, contributing to the high band degeneracy, as well as the nonexistence of compensating or killer intrinsic defects.<sup>45,49</sup> In contrast, CoSbSe and CoSbTe, both of which are not isostructural to CoSbS, are metallic conduction type materials. Isoelectronic alloying by Se on the S site further reduces  $\kappa_{\text{lat}}$  and therefore increases *zT*.<sup>50–52</sup> The recent discovery of the colossal power factor of CoSbS single crystals over the cryotemperature range also motivated interest in condensed matter physics.<sup>53,54</sup>

Herein, we systematically investigated the influence of Te alloying on the microstructure and thermoelectric properties of Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS. It was found that the solute segregation mediated by Te alloying led to increased grain size, which resulted in anomalous transport properties. The carrier scattering mechanism was beneficially changed, leading to simultaneous increases in carrier mobility and power factor. Meanwhile, the thermal properties were slightly influenced due to the compromise between the introduced point defects and weakened grain boundary for phonon scattering. As a result, Ni and Te codoping in CoSbS significantly increased the power factor and *zT*, with maximum peak values of around 20.6  $\mu\text{W cm}^{-1} \text{K}^{-2}$  and 0.65, respectively, which highlights the prospects of this material for intermediate-temperature thermoelectric power generation.

## Experimental

### Materials

High-purity raw materials were directly weighed according to nominal composition Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS<sub>1-x</sub>Te<sub>x</sub> samples ( $x = 0, 0.02, 0.04, \text{ and } 0.06$ ), loaded into a ball-milling jaw in a glove-box, and finally subjected to a one-time ball milling process without stopping for 5 h (SPEX SamplePrep 8000 Mixer Mill). The obtained nanopowders were loaded into a graphite die and

sintered *via* a direct-current quick hot press system at 1023 K under a pressure of  $\sim 80$  MPa for 2 min.

### Phase and microstructure characterization

Phase structures were characterized by powder X-ray diffraction (PXRD, PANalytical X'Pert Pro) using Cu K $\alpha$  radiation. PXRD patterns revealed that the materials crystallized with an orthorhombic structure (*Pbca* space group) rather than in the *Pmn*2<sub>1</sub> space group (Fig. S1†). The obtained Rietveld refinement parameters proved the good quality of the sample data. The sample crystallinity was not apparently changed and there was no second phase observed for the Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS<sub>1-x</sub>Te<sub>x</sub> samples within the detection limit of the PXRD apparatus. Microstructural analysis was conducted using a scanning electron microscope (SEM, JEOL6330F) and a scanning transmission electron microscopy (STEM, Thermo, Talos F200X G2, USA) with a high-angle annular dark-field (HAADF) detector and energy dispersive spectroscopy (EDS) was also employed. TEM samples were prepared using a conventional Ar-ion milling process.

### Physical property measurements

Bar samples were cut from pressed disks and used for the simultaneous measurement of electrical resistivity ( $\rho$ ) and Seebeck coefficient (*S*) on a commercial system (ULVAC ZEM-3). The thermal conductivity  $\kappa_{\text{tot}}$  was calculated using  $\kappa_{\text{tot}} = DC_{\text{p}}d$ , where *D*, *C<sub>p</sub>*, and *d* are the thermal diffusivity, specific heat capacity, and density, respectively. The thermal diffusivity coefficient (*D*) and specific heat capacity (*C<sub>p</sub>*) were concurrently measured on disk samples on a laser flash system (Netzsch LFA 457, Germany). The sample density (*d*) was determined using the Archimedes method. The room-temperature Hall coefficient *R<sub>H</sub>* was measured using a PPMS (physical properties measurement system, Quantum Design) instrument. The Hall carrier concentration (*n<sub>H</sub>*) was obtained using  $n_{\text{H}} = 1/eR_{\text{H}}$  and the Hall carrier mobility ( $\mu_{\text{H}}$ ) was calculated using  $\sigma = e\mu_{\text{H}}n_{\text{H}}$ , where *e* is the electronic charge and  $\sigma$  is the electrical conductivity.

## Results and discussion

Previous density functional theory (DFT) calculations revealed that CoSbTe crystallizes in the *Pnn*2 space group and exhibits a semimetal band structure.<sup>55</sup> Therefore, Te alloying in CoSbS would decrease the bandgap accordingly (Fig. 1a). The charge carrier concentration *n<sub>H</sub>* increased gradually, with the room-temperature value increasing from  $7.9 \times 10^{20} \text{ cm}^{-3}$  for Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS to  $9.0 \times 10^{20} \text{ cm}^{-3}$  for Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS<sub>0.94</sub>Te<sub>0.06</sub> (Fig. 1b). Considering that S and Te have the same number of valence electrons, this may be related to the associated change in the intrinsic point defect, *e.g.*, the Te<sub>Sb</sub> antisite defect.<sup>48</sup> Surprisingly, we also observed an increasing trend in the charge carrier mobility  $\mu_{\text{H}}$ , *e.g.*, 2.2  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  for Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS and 2.5  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  for Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS<sub>0.96</sub>Te<sub>0.04</sub> (Fig. 1b). The simultaneous increases in both *n<sub>H</sub>* and  $\mu_{\text{H}}$  contribute towards increased electrical conductivity  $\sigma$ , *e.g.*, the room-temperature value increased from  $2.8 \times 10^4 \text{ S m}^{-1}$  for Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS up to  $3.4 \times 10^4 \text{ S m}^{-1}$  for Co<sub>0.94</sub>Ni<sub>0.06</sub>SbS<sub>0.94</sub>Te<sub>0.06</sub> (Fig. 1c). More

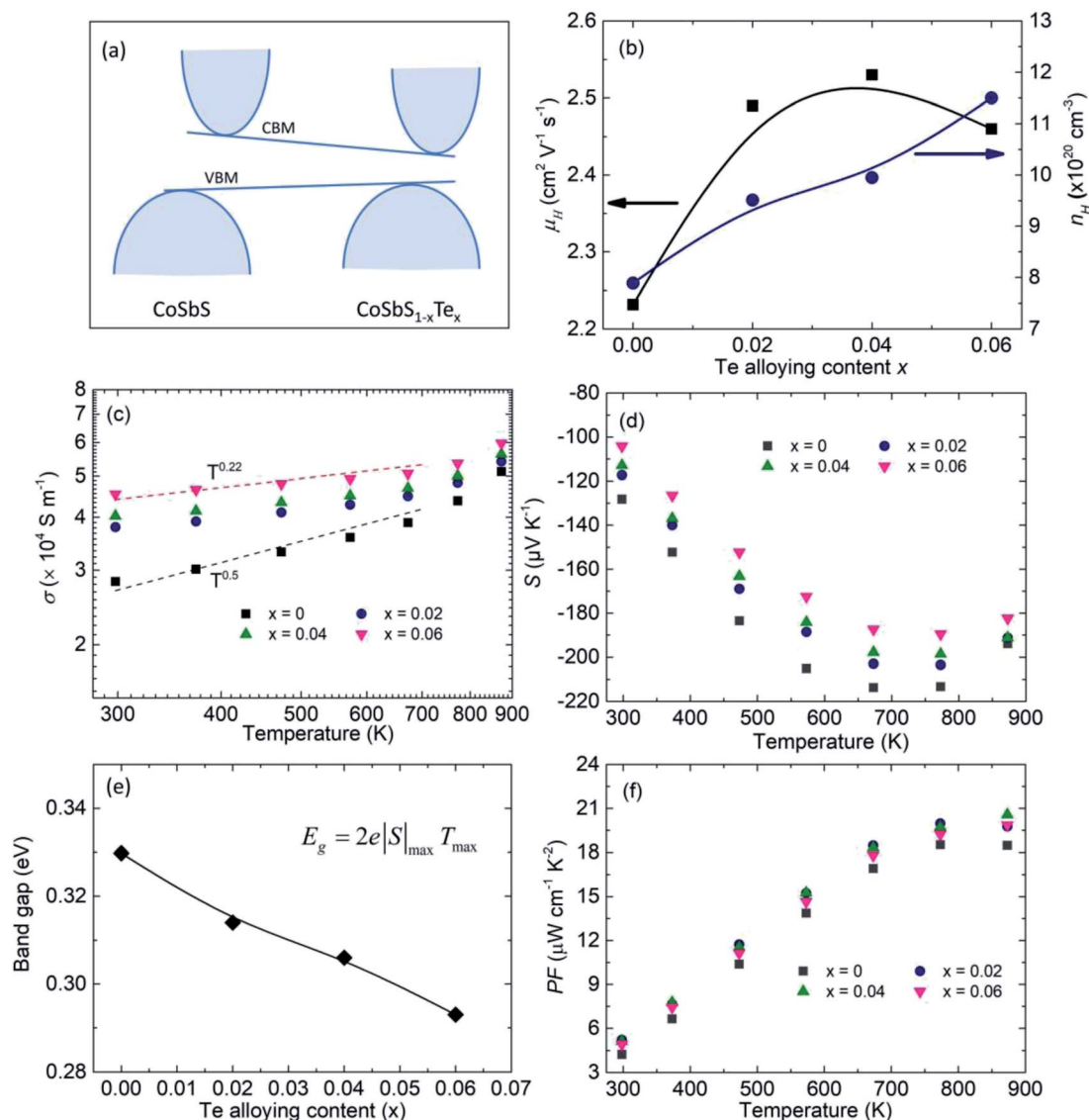


Fig. 1 Electronic properties of  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_{1-x}\text{Te}_x$  samples ( $x = 0, 0.02, 0.04,$  and  $0.06$ ). (a) Schematic diagram of band structure evolution after Te alloying in CoSbS, (b) charge carrier concentration  $n_{\text{H}}$  and carrier mobility  $\mu_{\text{H}}$  values at room temperature as a function of Te alloying content, (c and d) temperature-dependent electrical conductivity  $\sigma$  and Seebeck coefficient  $S$ , respectively, (e) the calculated bandgap based on the Goldsmid–Sharp method, and (f) the temperature-dependent power factor PF.

importantly, despite its high  $n_{\text{H}}$ ,  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}$  still exhibits a positive slope for the relationship between  $\sigma$  and  $T$ , which is the signature of an intrinsic semiconductor. This implies the occurrence of an additional carrier-scattering mechanism in CoSbS based materials in addition to acoustic phonon-carrier scattering and the high effective mass of carriers. This may include grain boundary scattering, impurity ionic scattering, and magnetic scattering.<sup>45</sup> It should be noted that Te alloying beneficially tunes the scattering mechanism, which can be ascribed to the weakened grain boundary scattering that will be discussed in the following. As expected, the Seebeck coefficient  $S$  is decreased after Te alloying due to the increased  $n_{\text{H}}$  (Fig. 1d). Due to the compromise between the increased  $n_{\text{H}}$  and the reduced  $E_{\text{g}}$ , the peak of  $S$  is maintained at around almost the same position. Based on the Goldsmid–Sharp band gap formula

$E_{\text{g}} = 2e|S|_{\text{max}}T_{\text{max}}$ , where  $|S|_{\text{max}}$  represents the maximum of absolute Seebeck coefficient and  $T_{\text{max}}$  is the temperature at which this value occurs, the observed decreasing trend after Te alloying is consistent with previous DFT calculations (Fig. 1e). Consequently, Te alloying leads to an increase in the power factor PF, with a maximum peak value of around  $20.6 \mu\text{W cm}^{-1} \text{K}^{-2}$  (Fig. 1f).

To further unveil the underlying mechanism of the unusual electronic properties after Te alloying, the single parabolic band (SPB) model was utilized for analysis herein. Based on the Pisarenko plot, namely the  $n_{\text{H}}$  dependent  $S$ , it is observed that the data of CoSbS-based samples, including Ni and Te codoping, as well as Ni doping,<sup>46</sup> are located around the obtained line with a total density of states effective mass  $m^* = 6m_{\text{e}}$  (Fig. 2a). This indicates that there is no significant change in the

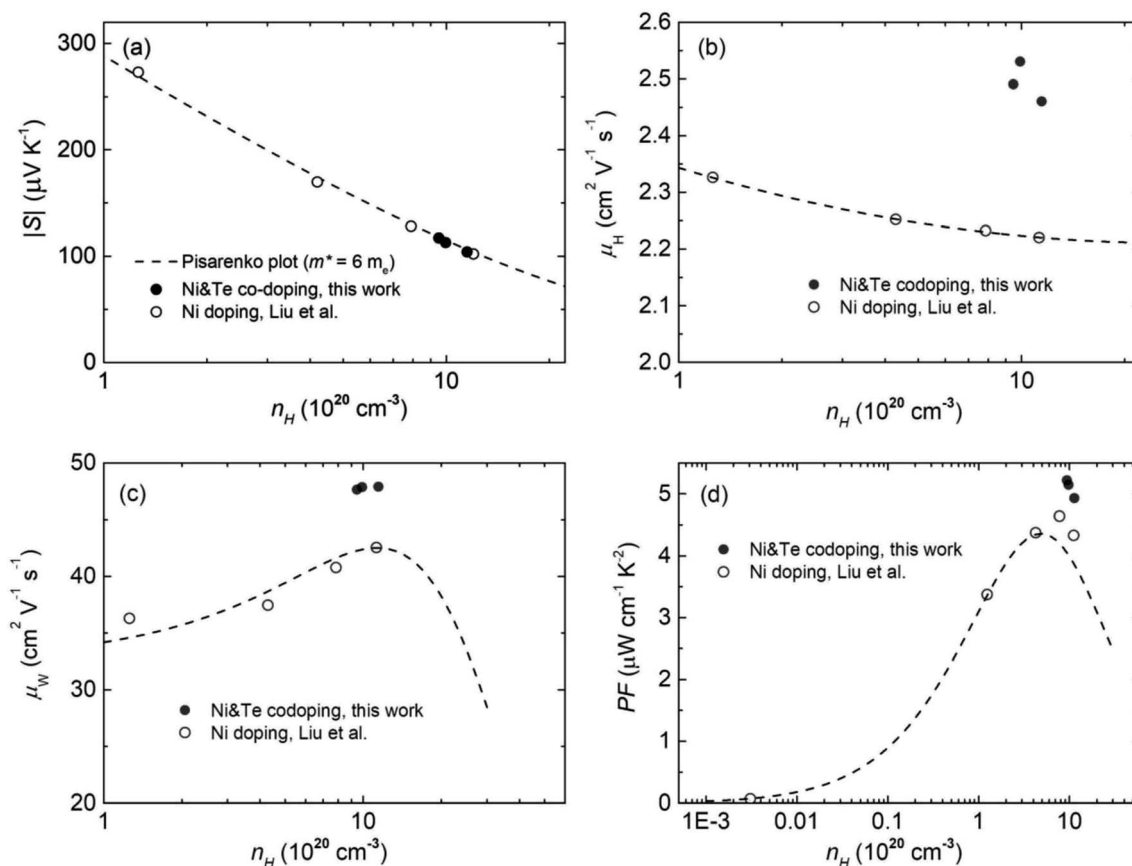


Fig. 2 Charge carrier concentration  $n_H$  dependent room-temperature electronic properties of the  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{Sb}_{1-x}\text{Te}_x$  samples ( $x = 0, 0.02, 0.04, \text{ and } 0.06$ ), in comparison to Ni doped  $\text{CoSbS}$ . (a) The Pisarenko plot, (b, c and d) the charge carrier mobility  $\mu_H$  values, the predicted weighted mobility  $\mu_w$ , and the power factor PF, respectively. The dashed lines were obtained based on a single parabolic band (SPB) model with a total effective mass of  $m^* = 6m_e$ .

conduction band minimum around the Fermi level, which indicates the effectiveness of the rigid band model. Our present conclusion is consistent with previous first-principle calculations that also revealed the unchanged band structure in  $\text{CoSbS}_{1-x}\text{Te}_x$ .<sup>50</sup> Compared to Ni doping, Ni and Te codoping leads to a higher  $\mu_H$  at the same  $n_H$  (Fig. 2b). In thermoelectrics, the weighted mobility  $\mu_w$ , irrespective of the doping element and/or  $n_H$ , can be well used to evaluate the ability of a material's electronic properties,<sup>25,56</sup> which is codetermined by the drift mobility  $\mu_D$  and the  $m^*$ , as shown in the following equation:

$$\mu_w = \mu_D \left( \frac{m^*}{m_e} \right)^{3/2} \quad (1)$$

where  $m_e$  is the electron mass. Herein, we used the simplified model to calculate the  $\mu_D$  and  $\mu_w$ .<sup>57</sup> It is found that Ni and Te codoped samples possess a higher  $\mu_w$  than Ni doped samples at the same  $n_H$  (Fig. 2c). Similarly, a higher PF is achieved for Ni and Te codoped samples, consistent with the tendency of  $\mu_w$  (Fig. 2d). All the above mentioned analysis indicates the anomalous electronic properties observed for Ni and Te codoping that are beyond the conventional SPB model.

Considering the almost unchanged band structure, grain boundary scattering should be the most plausible reason to

account for the unusual properties. Therefore, the average grain size was analyzed by SEM characterization on the freshly fractured surfaces of samples of  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}$  and  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{0.96}\text{Te}_{0.04}$ , respectively (Fig. 3a and c).  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}$  sample has an average grain size of around  $0.36 \mu\text{m}$  (Fig. 3b), which increased up to around  $0.57 \mu\text{m}$  after Te alloying (Fig. 3d). Moreover, the grain size distribution changed from unimodal to bimodal, indicating that Te alloying leads to inhomogeneous grain growth, namely abnormal grain growth characteristics. Therefore, the corresponding underlying mechanism is due to the increased grain boundary energy for some specific grain boundaries after Te alloying.

In metallurgy and ceramics science, it is widely acknowledged that impurities and alloying elements can significantly alter boundary energetics since these solute elements tend to be easily segregated along grain boundaries.<sup>58</sup> A well-known example is doped alumina, in which these segregated solute atoms alter the local bonding environment and thereby affect microstructure evolution.<sup>59,60</sup> The origin of abnormal grain growth behavior is assumed to be related to nonuniform grain boundary mobility,<sup>61</sup> due to the appearance of wetting phases along the grain boundary.<sup>24,62</sup> To have a deep understanding of microstructural evolution in Te-alloyed  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}$ , we

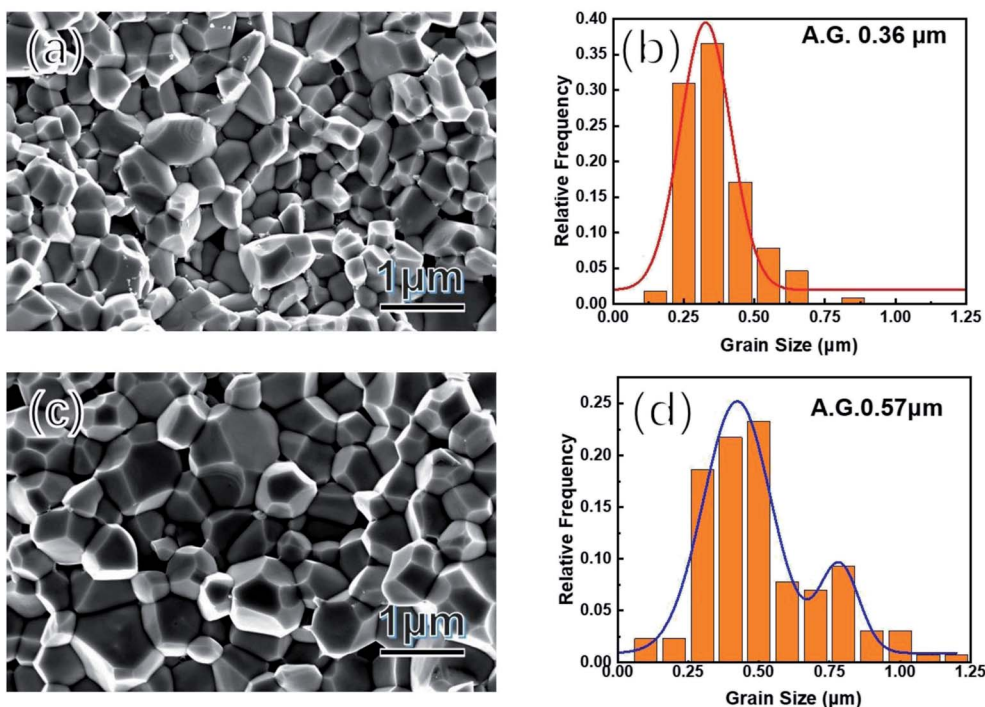


Fig. 3 (a and c) SEM images of freshly fractured surfaces of  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}$  and  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{0.96}\text{Te}_{0.04}$ , respectively; (b and d) their corresponding grain-size distribution analysis.

performed a thorough characterization on the  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{0.96}\text{Te}_{0.04}$  sample based on HAADF-STEM analysis, because the contrast in HAADF-STEM images is strongly dependent on the atomic number. Most of the precipitates were observed to occur around the grain boundary in the nanosized range with a low concentration (Fig. 4a), which are consistent with the sample composition and PXRD refinement results. It should be noted that these spherical-shaped particles in the grain, consisting of Si, C, O elements, are formed during the sample preparation process of the TEM observations. Grain boundaries with high energy are preferential locations for solute segregation that could lower the total energy and promote precipitation behavior at the grain boundary. Coupled with the chemical composition analysis (STEM-EDS), elemental Te segregates modestly to the grain boundary by means of precipitation (Fig. 4b). Considering the similar atomic numbers of Sb and Te, this means that the Te element is dominant (or as the elemental precipitate) in this precipitated compound. By checking the binary Sb–Te phase diagram, the highest possibility of this precipitate is therefore elemental Te, since there is no Te-rich compound near the end of this diagram. Since Te element has a relatively low melting point of 723 K, the segregation along the grain boundary acts as the ‘wetting phase’ character that could lead to grain growth *via* liquid phase sintering. From the viewpoint of chemical bonding, the substitution of S atoms with Te atoms leads to the smaller difference in atom electronegativity, corresponding to weaker polar bonding strength around the grain boundary, therefore promoting grain growth. Moreover, since we used the high-energy balling method in combination with the SPS technique to synthesize the nanostructured

thermoelectric materials with an average grain size of 0.36  $\mu\text{m}$ , structural instabilities derived from a high number of grain boundaries provided the driving force for grains to reduce the total area of grain boundaries and in turn suppress the excess free energy per unit.

Despite the big difference in the measured  $n_{\text{H}}$  after Te alloying, the  $\kappa_{\text{tot}}$  of the  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{1-x}\text{Te}_x$  samples reduces slightly over the low-temperature range (Fig. 5a), whereas Te alloying suppresses the bipolar effect above 673 K due to the remarkably increased  $n_{\text{H}}$ . Herein, we used the single parabolic band (SPB) model approximation with acoustic phonon scattering to calculate the Lorenz number ( $L$ ). After subtracting the electronic thermal conductivity  $\kappa_{\text{ele}} = L\sigma T$  from  $\kappa_{\text{tot}}$ , the calculated lattice thermal conductivity  $\kappa_{\text{lat}}$  is found to dominate the  $\kappa_{\text{tot}}$  and therefore shows a similar trend to  $\kappa_{\text{tot}}$  (Fig. 5b). Remarkably, Te alloying has an extremely weak influence on  $\kappa_{\text{lat}}$ . To further assess the theoretical contribution of phonon scattering from point defects, the Callaway–Debye model was used here,<sup>7,63</sup> as in the following:

In terms of a material containing substitutional defects, namely  $\text{CoSbS}_{1-x}\text{Te}_x$  samples, the relationship between the  $\kappa_{\text{lat}}$  and  $\kappa_{\text{lat,p}}$  of the pure  $\text{CoSbS}$  sample can be written as:

$$\frac{\kappa_{\text{lat}}}{\kappa_{\text{lat,p}}} = \frac{\tan^{-1}(u)}{u} \quad (2)$$

Here the parameter  $u$  is defined by:

$$u = \left( \frac{\pi^2 \theta_{\text{D}} \Omega}{h v_{\text{a}}^2 \kappa_{\text{lat,p}} \Gamma} \right)^{\frac{1}{2}} \quad (3)$$

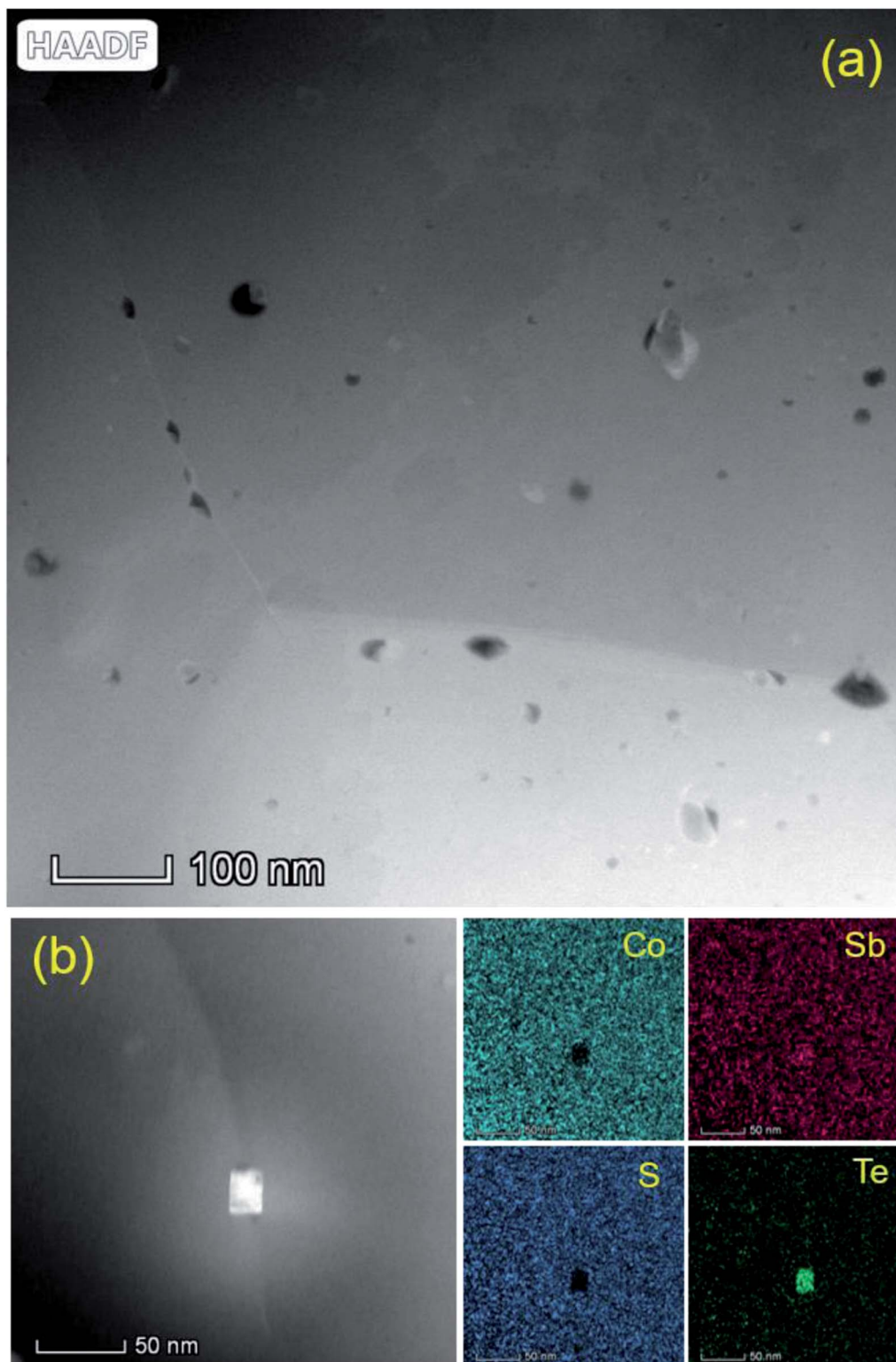


Fig. 4 (a) The high-resolution HAADF-STEM image around the grain boundary and (b) the high-resolution HAADF-STEM image and EDS mapping of the elemental segregation along the grain boundary.

where  $\Omega$  and  $h$  represent the average volume per atom and Planck constant, respectively, and the average sound velocity  $v_a$  can be calculated from:<sup>4-7</sup>

$$v_a = \left( \frac{1}{3} \left[ \frac{1}{v_1^3} + \frac{2}{v_s^3} \right] \right)^{-\frac{1}{3}} \quad (4)$$

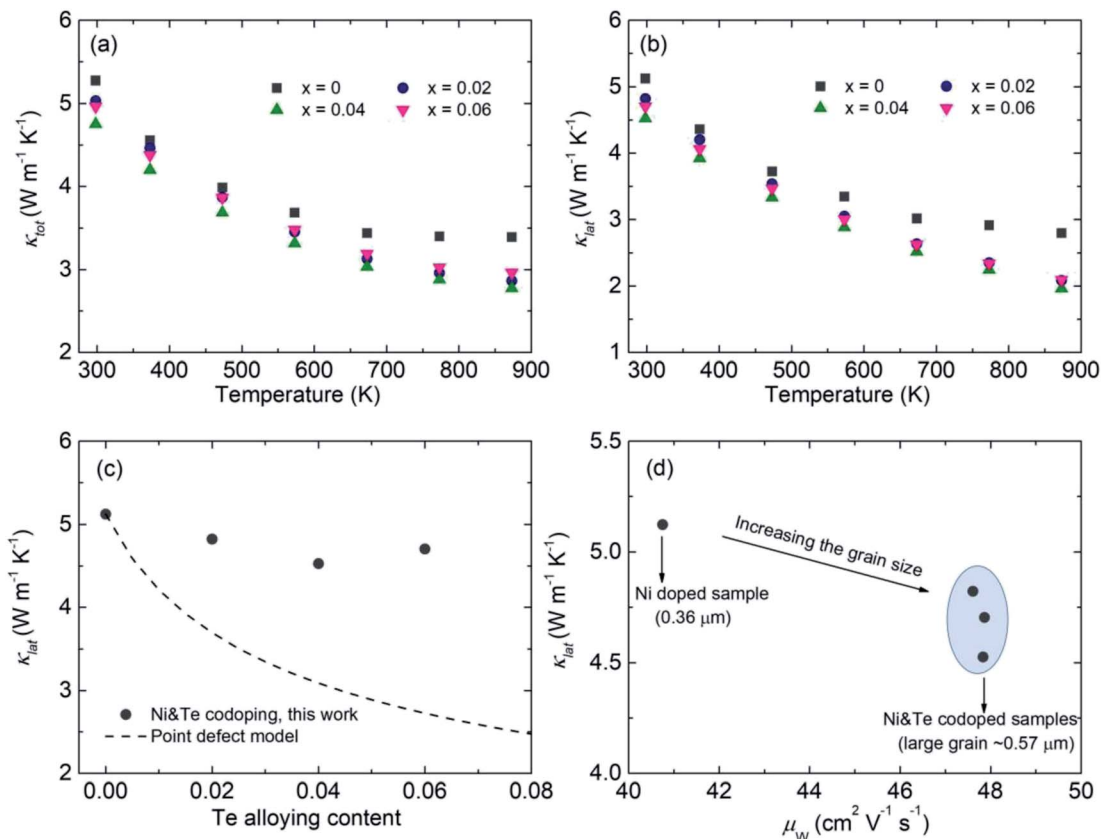


Fig. 5 Thermal properties results and analysis of the  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{1-x}\text{Te}_x$  samples ( $x = 0, 0.02, 0.04, \text{ and } 0.06$ ). (a and b) Temperature-dependent total thermal conductivity  $\kappa_{\text{tot}}$  and lattice thermal conductivity  $\kappa_{\text{lat}}$ , respectively, (c) comparison of the measured and simulated lattice thermal conductivity  $\kappa_{\text{lat}}$  as a function of Te alloying content, where the dashed line represents the theoretical value based on the Callaway–Debye model, and (d) the relationship between the calculated lattice thermal conductivity  $\kappa_{\text{lat}}$  and weighted carrier mobility  $\mu_{\text{w}}$  in  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{1-x}\text{Te}_x$ .

Here, the longitudinal ( $v_l$ ,  $5878 \text{ m s}^{-1}$ ) and transverse ( $v_s$ ,  $3542 \text{ m s}^{-1}$ ) sound velocities were used in eqn (3) and the obtained  $v_a$  was around  $3917 \text{ m s}^{-1}$ . The Debye temperature  $\theta_D$  can be calculated using:

$$\theta_D = \frac{h}{k_B} \left[ \frac{3N}{4\pi V} \right]^{\frac{1}{3}} v_a \quad (5)$$

where the  $V$  is the unit-cell volume,  $N$  is the number of atoms in a unit cell, and  $k_B$  is the Boltzmann parameter. The obtained  $\theta_D$  is around  $454 \text{ K}$ . The imperfection scaling parameter  $\Gamma$  in eqn (2) represents the strength of phonon scattering from point defects, including two components, the scattering parameter  $\Gamma_M$  due to mass fluctuation and the scattering parameter  $\Gamma_S$  due to strain field fluctuation. A phenomenological adjustable parameter  $\varepsilon$  is included to better estimate  $\Gamma_S$ , which can be derived from:

$$\varepsilon = \frac{2}{9} \left( \frac{6.4 \times \gamma(1 + v_p)}{(1 - v_p)} \right)^2 \quad (6)$$

$$v_p = \frac{1 - 2 \left( \frac{v_s}{v_l} \right)^2}{2 - 2 \left( \frac{v_s}{v_l} \right)^2} \quad (7)$$

$$\gamma = \frac{3}{2} \left( \frac{1 + v_p}{2 - 3v_p} \right) \quad (8)$$

where  $v_p$  is the Poisson ratio, with a value of  $0.22$ , the Gruneisen parameter ( $\gamma$ ) was calculated to be around  $1.34$ , and the phenomenological adjustable parameter  $\varepsilon$  is around  $39$ .

No compositional change occurs on the sites of Co and Sb,  $\Gamma_{\text{Co}} = \Gamma_{\text{Sb}} = 0$ , and the substitution between S and Te gives:

$$\Gamma_{\text{CoSbS}_{1-x}\text{Te}_x} = \frac{1}{3} \left( \frac{M_{(\text{S,Te})}}{M} \right)^2 \Gamma_{(\text{S,Te})} \quad (9)$$

$$\Gamma = \Gamma_M + \Gamma_S \quad (10)$$

$$\Gamma_{(\text{S,Te})} = \Gamma_{M,(\text{S,Te})} + \varepsilon \Gamma_{S,(\text{S,Te})} \quad (11)$$

$$\Gamma_{M,(\text{S,Te})} = x(1-x) \left( \frac{\Delta M}{M_{(\text{S,Te})}} \right)^2 \quad (12)$$

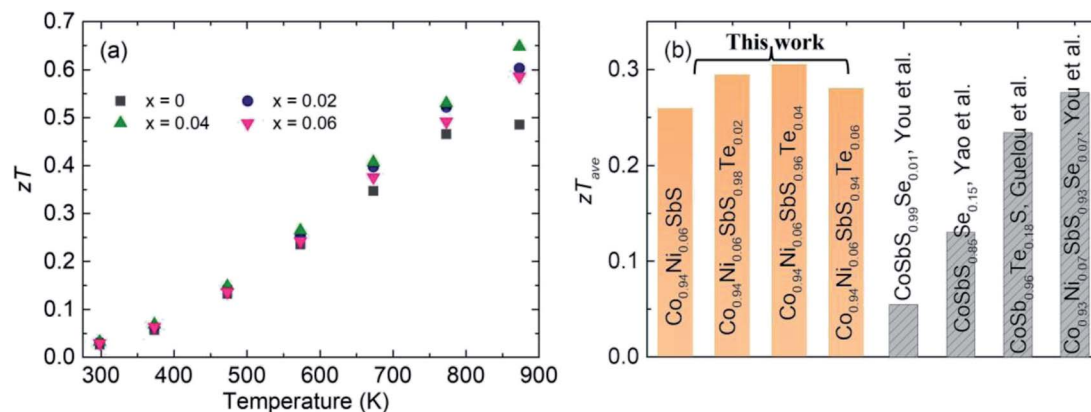


Fig. 6  $zT$  value of the  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{1-x}\text{Te}_x$  samples ( $x = 0, 0.02, 0.04$ , and  $0.06$ ). (a) Temperature-dependent  $zT$  values and (b) comparison of the  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{1-x}\text{Te}_x$  samples with other reported  $\text{CoSbS}$  samples prepared by Hou et al., Yao et al., and Guelou et al.

where  $\Delta M = M_{\text{Te}} - M_{\text{S}}$  and  $M_{(\text{S,Te})} = (1 - x)M_{\text{S}} + xM_{\text{Te}}$

$$\Gamma_{\text{S,(Te,S)}} = x(1 - x) \left( \frac{\Delta r}{r_{(\text{Te,S})}} \right)^2 \quad (13)$$

where  $\Delta r = r_{\text{Te}} - r_{\text{S}}$  and  $r_{(\text{Te,S})} = (1 - x)r_{\text{S}} + xr_{\text{Te}}$  then,

$$\Gamma_{(\text{Te,S})} = x(1 - x) \left[ \left( \frac{\Delta M}{M_{(\text{Te,S})}} \right)^2 + \varepsilon \left( \frac{\Delta r}{r_{(\text{Te,S})}} \right)^2 \right] \quad (14)$$

and then,

$$\Gamma_{\text{CoSbS}_{1-x}\text{Te}_x} = \frac{1}{3} \left( \frac{M_{(\text{Te,S})}}{M} \right)^2 x(1 - x) \left[ \left( \frac{\Delta M}{M_{(\text{Te,S})}} \right)^2 + \varepsilon \left( \frac{\Delta r}{r_{(\text{Te,S})}} \right)^2 \right] \quad (15)$$

Based on the above eqn (2)–(15), the obtained  $\kappa_{\text{lat}}$  of defective  $\text{CoSbS}$  containing substitutional  $\text{Te}$  defects at the  $\text{S}$  sites is shown as a dashed line in Fig. 5c. Apparently, the slight reduction in  $\kappa_{\text{lat}}$  after  $\text{Te}$  alloying is beyond the prediction based on the conventional Callaway–Debye model. Since the atomic mass of the impurity atom  $\text{Te}$  ( $127.6 \text{ g mol}^{-1}$ ) is much larger than that of the host atom  $\text{S}$  ( $32.06 \text{ g mol}^{-1}$ ), the calculated imperfection scaling parameter from the strain field fluctuation was higher than that of the mass fluctuation considering the similar atomic radii of  $\text{S}$  (102 pm) and  $\text{Te}$  (135 pm) (Fig. S2†). Here, it should be noted that the additional scattering mechanism may lead to an overestimated  $\kappa_{\text{lat}}$ .<sup>64</sup> In contrast, due to their larger grain sizes,  $\text{Ni}$  and  $\text{Te}$  codoped samples exhibit higher  $\mu_{\text{W}}$  and lower  $\kappa_{\text{lat}}$  values than  $\text{Ni}$ -doped samples, which follows conventional thinking and is therefore distinct from the unusual findings on the  $\text{Mg}_3(\text{Sb,Bi})_2$  system. The overestimated  $\kappa_{\text{lat}}$  value of defective  $\text{CoSbS}$  based on the point-defect model was due to the significantly increased grain size after  $\text{Te}$  alloying that weakens the grain boundary scattering. Therefore, alloying dopant-mediated grain growth leads to anomalous thermoelectric properties that are beyond conventional thermoelectric prediction models.

Due to the increased PF and suppressed  $\kappa_{\text{tot}}$ ,  $\text{Te}$  alloying leads to enhanced  $zT$  across the entire measured temperature

range, in which the peak  $zT$  value at 873 K is increased from 0.47 to 0.65 (Fig. 6a). Meanwhile, the highest average  $zT \sim 0.31$  is achieved for  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{0.98}\text{Te}_{0.02}$ , higher than those of other optimized  $\text{CoSbS}$ -based samples (Fig. 6b). Our results thus show the potential of using  $\text{CoSbS}$ -based samples for power generation at intermediate temperatures.

## Conclusions

In summary, we observed a novel phenomenon of solute segregation along the grain boundary of alloying mediated grain growth in  $\text{Co}_{0.94}\text{Ni}_{0.06}\text{SbS}_{1-x}\text{Te}_x$  samples, which led to anomalous thermoelectric properties. Specifically, the average grain size was increased from  $0.36 \mu\text{m}$  to  $0.57 \mu\text{m}$  after  $\text{Te}$  alloying. Due to the weakened strength of grain boundary scattering for electrons and phonons, the carrier mobility was increased while the lattice thermal conductivity was slightly suppressed. As a result,  $\text{Ni}$  and  $\text{Te}$  codoping in  $\text{CoSbS}$  significantly increased the power factor and  $zT$ , with maximum peak values of around  $20.6 \mu\text{W cm}^{-1} \text{ K}^{-2}$  and 0.65, respectively. Our work highlights the significance of solute segregation on thermoelectric properties that are beyond conventional thermoelectric model prediction.

## Author contributions

Weihong Gao: investigation; methodology; writing – original draft, Yuxi Yang, Mingqi Deng, Bin Sun, Yixuan Li: investigation; validation; writing – reviewing and editing; Yudong Fu, Zihang Liu, Jiehe Sui: conceptualization; supervision; funding acquisition; writing – reviewing and editing.

## Conflicts of interest

There are no conflicts to declare.



## Acknowledgements

This work was supported by the “Ten Thousand Million” Engineering Science and Technology Major Special Project of Heilongjiang Province (2019ZX10A01). It was also funded by the National Natural Science Foundation of China (No. 52130106, 51871082, and 52101247). The support from the Central University Basic Research Fund of China (FRFCU5710053021 and HIT.OCEF.2021014) is gratefully acknowledged.

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