Twin Engineering in Solution-Synthesized Nonstoichiometric Cu$_5$FeS$_4$ Icosahedral Nanoparticles for Enhanced Thermoelectric Performance

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A facile colloidal solution method has been developed for the fast, scalable synthesis of orthorhombic@cubic core–shell nonstoichiometric Cu$_5$FeS$_4$ icosahedral nanoparticles. Such nanoparticles contain high-density twin boundaries in the form of fivefold twins. Spark plasma sintering consolidates the nanoparticles into nanostructured pellets, which retain high-density twin boundaries and a tuned fraction of the secondary phase Fe-deficient cubic Cu$_5$FeS$_4$. As a result, the thermal and electrical transport properties are synergistically optimized, leading to an enhanced $zT$ of about 0.62 at 710 K, which is about 51% higher than that of single-phase Cu$_5$FeS$_4$. This study provides an energy-efficient approach to realize twin engineering in nonstoichiometric Cu$_5$FeS$_4$ nanomaterials for high-performance thermoelectrics.

1. Introduction

Declining fossil fuel reserves, together with ever-growing global energy demands, have stimulated the worldwide interests in high-performing energy conversion technologies.[1,2] Thermoelectrics, capable of directly converting thermal energy into electric energy, can be utilized to generate useful electricity from waste heat, thus possessing potential in alleviating the energy demands. The conversion efficiency of a thermoelectric material is determined by its dimensionless figure of merit ($zT$), $zT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ denote, respectively, the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity.[3–8] Recently, Cu-based sulfides have attracted extensive attention as potentially useful thermoelectric materials, due to their competitive $zT$ coupled with low toxicity and cost.[9–16] One of the promising candidates is Cu$_5$FeS$_4$ (also known as bornite) that exhibits complex cation order–disorder phase transitions upon heating, transforming from the orthorhombic phase ($Pbca$, $a = c = 10.95$ Å, $b = 21.86$ Å) through the intermediate cubic phase ($Fm\bar{3}m$, $a = 10.95$ Å) to the high cubic phase ($Fm\bar{3}m$, $a = 5.49$ Å), when heated from 300 K through 473 to 543 K.[$^{12}$] The high cubic phase possesses completely disordered distribution of Cu, Fe, and vacancies in the centers of S tetrahedrons, which largely disturbs phonon transport and results in low lattice thermal conductivity.[12] To improve electrical conductivity, nonstoichiometric bornite with more Cu and less Fe was synthesized, which demonstrated higher carrier concentration and an enhanced $zT$ of about 0.52 at 700 K.$^{13}$ Nevertheless, Cu$_5$FeS$_4$ has been primarily fabricated via high-temperature, energy-intensive method. Alternative low-cost, scalable solution synthesis has also been exploited to synthesize high-performance nonstoichiometric bornite ($zT \approx 0.56, 690$ K).[$^{17}$]

Defect engineering[$^{18–20}$] has proven effective to optimize the thermal[$^{21–27}$] and electronic[$^{28–35}$] properties of a diversity of thermoelectric materials. Defects, such as point defects, dislocations, and grain boundaries, can enhance scattering of phonons with varied mean free paths, reducing the lattice thermal conductivity ($\kappa_L$).[$^{21–26}$] Twin boundaries are expected to decrease $\kappa_L$ through enhanced phonon scattering, while exert minor influence on carrier mobility due to their ordered atomic arrangement.[36,37] These boundaries could also scatter low-energy carriers to improve the Seebeck coefficient, as demonstrated in twin-containing Bi$_0.5$Sb$_{1.5}$Te$_3$.[16] Therefore, twin engineering provides a potential strategy to synergistically
optimize the thermal and electrical transport properties. Few attempts combined melting spinning, ball milling, and spark plasma sintering (or hot pressing) to introduce twin boundaries into bulk materials (e.g., Bi₂Te₃, Cu-Ni alloy) yet without control on their density and never realized in Cu-based sulfide (e.g., Cu₅FeS₄). Although inexpensive solution synthesis is capable of controlling grain sizes in thermoelectric nanomaterials (and therefore grain boundaries in sintered compacts), controlling the formation and density of twin boundaries proves challenging. Hence, it is pivotal to develop a new strategy to realize the formation and control the density of twin boundaries in thermoelectric compounds.

Icosahedral nanocrystal represents a fascinating polyhedral structure that typically consists of 20 tetrahedral subunits separated by 30 twin boundaries and has a surface enclosed by 20 {111} crystal facets (for a cubic crystal structure). Synthesizing such icosahedral nanocrystals provides a potential controllable approach to introduce high-density twin boundaries into thermoelectric materials. However, the synthesis of icosahedral nanocrystals is primarily realized in cubic-structured metals and never in Cu₅FeS₄. Herein, we demonstrate the controllable solution synthesis of Cu₅FeS₄ icosahedral nanoparticles containing high-density twin boundaries through a fast, scalable colloidal synthesis method. Further, in order to tune the carrier concentration, we selectively grow Fe-deficient cubic Cu₅FeS₄ as the nanoparticle shell, leading to the formation of orthorhombic/cubic core–shell structures. The icosahedral core–shell nanoparticles can be sintered into nanostructured compacts retaining high density of twin boundaries and a tuned fraction of the cubic Cu₅FeS₄, leading to the synergistic optimization of electrical and thermal transport properties.

2. Results and Discussion

2.1. Characterization of Cu₅FeS₄ Icosahedral Nanoparticles

The solution synthesis of Cu₅FeS₄ icosahedral nanoparticles requires well-controlled experimental parameters, involving heating a mixture of a S-oleylamine (OLA) solution and a CuCl₂-Fe(acac)₃-OLA solution at 553 K for 30 min (see the Experimental Section; Figure S1, Supporting Information). Powder X-ray diffraction (PXRD) patterns (Figure 1a) can be indexed to mixed phases of orthorhombic Cu₅FeS₄ (denoted as orth-Cu₅FeS₄; PDF Card No. 42-0586) with lattice parameters a = c of ≈10.96 Å and b of ≈21.81 Å and cubic Cu₅FeS₄ (denoted as cubic-Cu₅FeS₄; PDF Card No. 24-0500) with a of ≈5.52 Å. The relation between their lattice parameters, that is, a(orth-Cu₅FeS₄) is close to 1/2 of a(orth-Cu₅FeS₄) and 1/4 of b(orth-Cu₅FeS₄), leads to the appearance of several “double peaks” in the PXRD patterns, for example, 111, 200, and 220 peaks of cubic-Cu₅FeS₄ are next to 242, 080, and 084 peaks of orth-Cu₅FeS₄, respectively. Scanning electron microscopy (SEM) images (Figure 1b, and Figure S2, Supporting Information) show that the product predominantly forms icosahedral nanoparticles that are bound by 20 triangular facets and reveal both fivefold and threefold symmetry (insets of Figure 1b,c). Transmission electron microscopy (TEM) images (Figure 1c, and Figure S3, Supporting Information) reveal projected hexagonal shape (due to that the viewing direction is close to the threefold axis direction) and confirm the particle size (the distance between two opposite “edges”) to be 70–180 nm. To evaluate the chemical composition of and element distribution in the nanoparticles, ultrathin sections from icosahedrons were prepared (see the Supporting Information). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Figure 1d) reveals the existence of Cu, Fe, and S with unevenly distributed Cu and Fe. The core is much richer in Fe than the shell while the shell contains more Cu, demonstrating a core–shell structure. Quantitative analysis based on EDS mappings (Figure S4, Table S1, Supporting Information) shows that the Cu:Fe:S atomic ratios are close to Cu₄8.1±1.5Fe₁3.6±1.5S₃8.1±2.7 and Cu₄6.8±2.7Fe₁3.1±1.9S₃1.1±2.2 for the core and shell, respectively, which are both nonstoichiometric Cu₅FeS₄ while the shell is Fe-deficient.
Selected area electron diffraction (SAED) patterns and high-resolution TEM (HRTEM) images were further collected to investigate the crystal structure of the core–shell structure. SAED pattern (Figure S5, Supporting Information) was collected from an icosahedron with the incident electron beam parallel to its fivefold axis, which demonstrates the fivefold symmetry and can be indexed to five SAED patterns along \([110]\) zone axis of cubic-Cu\(_5\)FeS\(_4\) (Figure S6, Supporting Information) superimposed together with four of them rotating at \(180^\circ/5\) \((n = 1, 2, 3, 4)\), respectively. To collect high-quality HRTEM images and distinguish the crystal structures of the core and shell, ultrathin sections of icosahedrons were selected for further TEM characterization. HRTEM image (Figure 2a) reveals high density of twin boundaries in the form of fivefold twins, and corresponding fast Fourier transformed (FFT) pattern of the ultrathin section reveals fivefold symmetry, indicating that the incident electron beam direction is parallel to the fivefold axis of the particle. These results indicate that in principle each icosahedral nanoparticle should consist of 20 tetrahedral subunits and therefore contain 30 twin boundaries, which is consistent with reported characterization results on cubic-structured metal icosahedral nanocrystals.\(^{[31,44]}\) Based on this, the twin boundary density is estimated to be \(1\mbox{–21} \times 10^{22} \mbox{ m}^{-3}\). Due to the similar crystal structure and close relation in lattice parameters between cubic- and orth-Cu\(_5\)FeS\(_4\), sharp interface between the core and shell were not observed. Nevertheless, FFT patterns collected from single-crystalline regions of the shell (Figure 2b) and core (Figure 2c), as shown in Figure 2d,e, respectively, are consistent with the simulated SAED patterns along \([110]\) zone axis of cubic-Cu\(_5\)FeS\(_4\) (Figure S6, Supporting Information) and \([210]\) zone axis of orth-Cu\(_5\)FeS\(_4\) (Figure S7, Supporting Information), respectively. HRTEM images (Figure 2b,c) give lattice spacings of 3.1 Å, which correspond to \((111)\) and \((242)\) planes of cubic- and orth-Cu\(_5\)FeS\(_4\), respectively. Combined with PXRD and EDS analyses, it is concluded that the synthesized icosahedrons are nonstoichiometric orthorhombic@cubic core–shell Cu\(_5\)FeS\(_4\) nanoparticles containing high-density twin boundaries.

### 2.2. Formation Mechanism of Cu\(_5\)FeS\(_4\) Icosahedral Nanoparticles

To understand the formation mechanism of the core–shell icosahedral nanoparticles, products synthesized after varied durations of heating (i.e., 10, 30, and 60 min) were investigated. PXRD (Figure 3a) reveals the product after 10 min of heating to be orth-Cu\(_5\)FeS\(_4\). SEM images (Figure 3b, and Figure S8, Supporting Information) of the as-synthesized nanoparticles, together with TEM images of ultrathin section of this sample (Figure 3c), reveal that the product is composed of nanoparticles attached by smaller particles with distinctive sizes of 70–140 and 10–20 nm, respectively. EDS elemental mapping (Figure 3d, and Figure S9, Supporting Information) demonstrates that apart from nanoparticles with uniform distribution of Cu, Fe, and S, nanoparticles with Fe-richer core and Cu-richer shell are formed as well. With increasing the heating duration to 30 min, icosahedral nanoparticles with Fe-rich core and Cu-rich shell are obtained. We speculate that S may combine with Fe more easily than Cu in our synthesis. The particle formed at the initial synthesis stage should be Fe-rich (i.e., the composition of the core); with prolonging the reaction duration, the newly formed Cu\(_5\)FeS\(_4\) phase should be Fe-deficient, as the Fe:Cu molar ratio of the remained precursors is less than 1:5. Eventually, the core–shell nanoparticles form, with the core being Fe-rich and the shell being Cu-rich. The low Fe concentration in the shell could be one of the reasons that lead to the formation of cubic-Cu\(_5\)FeS\(_4\) and we also notice that Fe-deficient cubic-Cu\(_5\)FeS\(_4\)
has been reported to be retained after solution synthesis. The morphology evolution process of Cu$_5$FeS$_4$ icosahedral nanoparticles is demonstrated in Figure 3e. When the heating was prolonged to 60 min, with expected growth of shell and nanoparticles, the product is determined to be mixed phases of ortho- and cubic-Cu$_5$FeS$_4$ with further increased fraction of the latter (Figure 3a). SEM (Figure S10, Supporting Information) reveals the product to be icosahedral nanoparticles and a small fraction of microsized polyhedrons.

2.3. Characterization of Cu$_5$FeS$_4$ Sintered Samples

The ability to synthesize Cu$_5$FeS$_4$ core–shell icosahedral nanoparticles with controlled morphology, composition, and defects in ~4 g quantities allowed the facile fabrication of sulfide pellets by spark plasma sintering (SPS) without the necessity of repeated solution preparation. Due to that nonstoichiometric, Fe-deficient Cu$_5$FeS$_4$ has higher electrical and thermal conductivity compared to nearly stoichiometric Cu$_5$FeS$_4$,[17] the phase fraction of cubic-Cu$_5$FeS$_4$ (Cu:Fe atomic ratio of 60.8 ± 2.7 : 6.1 ± 1.2) has been controlled by adjusting SPS temperature (i.e., 748 and 773 K, denoted as 30min-748K and 30min-773K, respectively), in order to obtain optimized thermoelectric performance. PXRD (Figure 4a, and Figure S11, Supporting Information) reveals that both pellets belong to mixed phases of ortho- and cubic-Cu$_5$FeS$_4$, and with increasing SPS temperature from 748 to 773 K, the fraction of cubic-Cu$_5$FeS$_4$ decreases significantly. With higher fraction of Fe-deficient cubic-Cu$_5$FeS$_4$, 30min-748K has much higher thermal conductivity compared to 30min-773K, leading to much lower $zT$ (Figure S12, Supporting Information). EDS elemental mapping (Figure S13, Supporting Information) shows that the 30min-773K pellet has more uniform distribution of Cu and Fe, indicating that SPS promoted the homogeneous distribution of both elements. This changed the composition of the shell (i.e., became less Fe-deficient) and resulted in the conversion to orth-Cu$_5$FeS$_4$ from cubic-Cu$_5$FeS$_4$.

SEM and TEM images (Figure 4b,c, and Figures S14 and S15, Supporting Information) reveal that the 30min-773K pellet is composed of nanoparticles that have similar particle sizes to the solution-synthesized products. Nanopores with nonuniform sizes were also observed. HRTEM image (Figure 4d) confirms the retaining of the fivefold symmetry and high-density twin boundaries in the form of fivefold twins. Such interfaces are expected to enhance phonon scattering, thus leading to the decrease of lattice thermal conductivity. For comparison, the products synthesized after heating for 10 and 60 min were also consolidated into pellets by SPS at 773 K (denoted as 10min-773K and 60min-773K, respectively). PXRD (Figure 4a) shows 10min-773K is pure orth-Cu$_5$FeS$_4$, while 60min-773K is composed of ortho- and cubic-Cu$_5$FeS$_4$. SEM images (Figure S16, Supporting Information) show that 10min-773K is composed principally of fine nanoparticles while 60min-773K consists of both polyhedrons and microsized particles, both resembling their solution-synthesized counterparts.

2.4. Thermoelectric Performance of Cu$_5$FeS$_4$ Sintered Samples

Figure 5 shows the thermoelectric performance of 10min-773K, 30min-773K, and 60min-773K as a function of...
temperature. The contrast in the temperature-dependent electrical conductivity ($\sigma$) for the different pellets is striking (Figure 5a). The $\sigma$ of 10min-773K (single-phase Cu$_5$FeS$_4$) increases from $\approx6.9 \times 10^2$ S m$^{-1}$ at 315 K to $\approx7.7 \times 10^2$ S m$^{-1}$ at 710 K. By contrast, 30min-773K, with a small fraction of more conductive Fe-deficient cubic-Cu$_5$FeS$_4$, demonstrates significantly enhanced $\sigma$ (from $\approx5.7 \times 10^3$ S m$^{-1}$ at 315 K to $\approx1.4 \times 10^4$ S m$^{-1}$ at 710 K). With the highest fraction of cubic-Cu$_5$FeS$_4$, 60min-773K reveals the largest $\sigma$, rising from $1.3 \times 10^4$ S m$^{-1}$ at 315 K to $2 \times 10^4$ S m$^{-1}$ at 465 K and remaining nearly constant at higher temperature up to 685 K. Hall measurements (Table 1) give a clear correlation between the Fe deficiency (e.g., fraction of cubic-Cu$_5$FeS$_4$) and carrier concentration ($n$). The higher $\sigma$ values ($\sigma = ne\mu$, $e$ is the electron charge) of 60min-773K and 30min-773K are consistent with their larger $n$. The highest carrier mobility ($\mu$) in 30min-773K indicates that twin boundaries have limited influence on carrier scattering. In fact, 60min-773K and 30min-773K obtain higher $\sigma$ values compared to Cu$_5$FeS$_4$ bulk materials fabricated via high-temperature method (Figure S17, Supporting Information).

The p-type behavior is observed in all the three pellets, indicated by their positive Seebeck coefficient ($S$) within the whole temperature range (Figure 5b). $S$ for 10min-773K increases from $\approx150$ $\mu$V K$^{-1}$ at 315 K to $\approx270$ $\mu$V K$^{-1}$ at 465 K, before decreasing to $\approx185$ $\mu$V K$^{-1}$ at 710 K. By contrast, $S$ for 30min-773K and 60min-773K both keep rising with increasing the temperature yet with lower values (e.g., $\approx170$ and $\approx155$ $\mu$V K$^{-1}$ at 710 K, respectively). Due to much better $\sigma$ values coupled with relatively high $S$, 30min-773K and 60min-773K possess enhanced power factors ($S^2\sigma$), $\approx0.39$ and $\approx0.45$ mW m$^{-1}$ K$^{-2}$ at 710 K that are $\approx50$ and $\approx70$% larger than that of 10min-773K, respectively (Figure 5c). This clearly demonstrates that introducing the Fe-deficient cubic-Cu$_5$FeS$_4$ is very effective in optimizing electronic properties and enhancing the $S^2\sigma$ of Cu$_5$FeS$_4$.

The variation in thermal conductivity ($\kappa$) with temperature for 10min-773K and 30min-773K is very similar, maintaining very low values within the whole temperature range. $\kappa$ for 30min-773K (10min-773K) decreases from $\approx0.43 \approx0.42$ W m$^{-1}$ K$^{-1}$ at 300 K to $\approx0.31 \approx0.31$ W m$^{-1}$ K$^{-1}$ at 475 (525) K, before rising to $\approx0.45 \approx0.46$ W m$^{-1}$ K$^{-1}$ at 710 K. These $\kappa$ values are relatively low compared to other examples of Cu$_5$FeS$_4$ bulk counterparts fabricated through high-temperature synthesis and ball milling.[12,46,67] By contrast, $\kappa$ for 60min-773K reveals much higher values, decreasing from $\approx0.52$ W m$^{-1}$ K$^{-1}$ at room temperature to $\approx0.48$ W m$^{-1}$ K$^{-1}$ at 375–475 K before rising to $\approx0.68$ W m$^{-1}$ K$^{-1}$ at 710 K.

Lattice thermal conductivity ($\kappa_L$) was estimated by subtracting $\kappa$ (Figure S18, Supporting Information) from $\kappa$, as shown in Figure 5e. Among all the pellets, 30min-773K possesses the lowest $\kappa_L$ within the whole temperature range, decreasing from $\approx0.39$ W m$^{-1}$ K$^{-1}$ at 300 K to $\approx0.23$ W m$^{-1}$ K$^{-1}$ before rising to $\approx0.29$ W m$^{-1}$ K$^{-1}$ at 710 K. The increasing value of $\kappa_L$ at higher temperature is related to the phase transformation of Cu$_5$FeS$_4$ to high-temperature cubic phase. Two notable comparisons can be made. (1) $\kappa_L$ for 30min-773K at 710 K is lower compared to that of 10min-773K, although 10min-773K has relatively smaller crystallite size. This clearly demonstrates that twin boundaries can effectively enhance acoustic phonon scattering and significantly reduce the $\kappa_L$. (2) $\kappa_L$ for 30min-773K at 710 K is lower than that of 60min-773K although both possess twin boundaries. The increased grain size and/or the higher concentration of cubic-Cu$_5$FeS$_4$ with higher $\kappa_L$ in 60min-773K should be responsible for this.

The optimized electrical properties coupled with the lower $\kappa_L$ result in excellent $zT$ values in 30min-773K, for example, $\approx0.62$ at 710 K that is $\approx51$ and $\approx33$% higher than those of single-phase Cu$_5$FeS$_4$ pellet (10min-773K) and orthorhombic cubic-Cu$_5$FeS$_4$ pellet (60min-773K), respectively. The contrast in thermoelectric performance between the pellets underscores the importance of defect engineering, for example, formation of high-density twin boundaries (included in icosaehedral nanoparticles) and stoichiometry control (via...
introducing Fe-deficient cubic-Cu$_5$FeS$_4$. Notable is that $zT$ for 30min-773K at 710 K compares very favorably with those for Cu-Fe-S compounds reported previously (Table 2). Therefore, it is achievable to synthesize twin-engineered, composition-tunable, and high-performance Cu$_5$FeS$_4$ via sustainable solution methods. In principle, the present method could be extended to the synthesis of new doped Cu$_5$FeS$_4$ nanomaterials (e.g., Se doping)\(^{[47]}\) to achieve better performance.

Figure 5. Thermoelectric properties of Cu$_5$FeS$_4$ pellets 10min-773K, 30min-773K, and 60min-773K: a) $\sigma$, b) $S$, c) $S^2\sigma$, d) $\kappa$, e) $\kappa_l$, and f) $zT$ as a function of temperature.

Table 1. A summary of electronic properties, room-temperature Hall carrier concentration ($n_H$) and mobility ($\mu_H$), and lattice thermal conductivity ($\kappa_l$) of the pellets.

<table>
<thead>
<tr>
<th>Pellet</th>
<th>$n_H$</th>
<th>$\mu_H$</th>
<th>$\kappa_l$</th>
<th>$zT$</th>
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<tr>
<td>10min-773K</td>
<td>6.9 $\times$ 10$^4$</td>
<td>150</td>
<td>1.8</td>
<td>0.24</td>
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<tr>
<td>30min-773K</td>
<td>5.6 $\times$ 10$^4$</td>
<td>68</td>
<td>6.5</td>
<td>0.55</td>
</tr>
<tr>
<td>60min-773K</td>
<td>1.3 $\times$ 10$^4$</td>
<td>56</td>
<td>41</td>
<td>0.20</td>
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</table>
Table 2. A summary of thermoelectric properties of Cu-Fe-S compounds.

<table>
<thead>
<tr>
<th>Materials</th>
<th>zT$^a$ [K]</th>
<th>zT$^b$</th>
<th>S$^c$σ$^d$ [mW m$^{-1}$ K$^{-2}$]</th>
<th>κ$^e$ [W m$^{-1}$ K$^{-1}$]</th>
<th>Synthesis method</th>
<th>References</th>
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<tr>
<td>Cu$_5$Fe$_2$S$_4$</td>
<td>710</td>
<td>0.62</td>
<td>0.45</td>
<td></td>
<td>Colloidal synthesis+SPS</td>
<td>This work</td>
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<td>Cu$_5$Fe$_2$S$_4$</td>
<td>700</td>
<td>0.38</td>
<td>0.25</td>
<td>0.485</td>
<td>Melting+annealing+SPS</td>
<td>[12]</td>
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<tr>
<td>Cu$_5$Fe$_2$S$_4$</td>
<td>700</td>
<td>0.52</td>
<td>0.35</td>
<td>0.49</td>
<td>Melting+annealing+SPS</td>
<td>[12]</td>
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<tr>
<td>Cu$_5$Fe$_2$S$_4$</td>
<td>543</td>
<td>0.35</td>
<td>0.34</td>
<td>0.33</td>
<td>Ball milling+hot pressing</td>
<td>[46]</td>
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<td>Cu$_5$Fe$_2$S$_4$</td>
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<td>0.56</td>
<td>0.4</td>
<td>0.47</td>
<td>Colloidal synthesis+SPS</td>
<td>[17]</td>
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<td>Cu$_5$Fe$_2$S$_4$</td>
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<td>0.5</td>
<td>0.43</td>
<td>0.47</td>
<td>Ball milling+SPS</td>
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<td>0.26</td>
<td>0.84</td>
<td>2.08</td>
<td>Melting+annealing+SPS</td>
<td>[11]</td>
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<tr>
<td>Cu$_5$Fe$_2$S$_4$</td>
<td>630</td>
<td>0.17</td>
<td>0.46</td>
<td>1.66</td>
<td>Melting+annealing+PAS$^i$</td>
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<td>0.439</td>
<td>Solution synthesis+hot pressing</td>
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<td>Mechanical alloying+SPS</td>
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<td>Ball milling+SPS</td>
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<td>0.07</td>
<td>1.1</td>
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<td>[14]</td>
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<td>Cu$_5$Fe$_2$S$_4$</td>
<td>675</td>
<td>0.22</td>
<td>0.55</td>
<td>1.6</td>
<td>Melting+annealing+SPS</td>
<td>[13]</td>
</tr>
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</table>

$^a$The temperature at which maximum $zT$ was achieved; $^b$zT, S$^c$σ$^d$, and κ$^e$ at T; $^i$Plasma-activated sintering.

3. Conclusion

In summary, a colloidal solution method realizes the quick and large-scale synthesis of orthorhombic@cubic core–shell Cu$_5$Fe$_2$S$_4$ icosahedral nanoparticles with high-density twin boundaries and nonstoichiometric composition. Spark plasma sintering of the nanoparticle produces nanostructured pellets. The thermal and electrical transport properties have been synergistically optimized due to inclusion of the high-density twin boundaries and a tuned fraction of Fe-deficient cubic-structured Cu$_5$Fe$_2$S$_4$, resulting in an enhanced $zT$ value of $≈0.62$ at 710 K. This study offers an energy-efficient route to high performing, twin-engineered, nonstoichiometric Cu$_5$Fe$_2$S$_4$ thermoelectric nanomaterials.

4. Experimental Section

**Materials Synthesis**: 50 mmol S powder was added to 150 mL OLA that was heated to 333 K and held for 6 h to yield a brown S-OLA solution. In parallel, 50 mmol CuCl$_2$ and 10 mmol Fe(acac)$_3$ were added to 100 mL OLA within a three-neck round-bottom flask. The solution was stirred for 6 h at room temperature under N$_2$ flow, heated to 453 K in 5 min, and held for 10 min to get a dark brown homogeneous solution. After the CuCl$_2$:Fe(acac)$_3$:OLA solution was heated to 553 K in 3 min, the freshly prepared 150 mL S-OLA solution was rapidly poured into the solution under N$_2$. The mixture was heated to 553 K again, held for either 10, 30, or 60 min and allowed to cool to 333 K under N$_2$. The brown-black products were washed with hexane and ethanol, and then dispersed in a mixture of hydrazine and hexane to remove coated organic ligands. The hydrazine-treated nanoparticles were collected and dried under vacuum for 3 h at 333 K. Powders were densified in a graphite die using SPS (uniaxial pressure of $≈$45 MPa; 773 K; 3 min).

**Materials Characterization and Performance Evaluation**: PXRD patterns were collected by a PANalytical X’pert diffractometer (Cu K$_\alpha$ radiation, $\lambda = 1.5406$ Å). The morphology of products was investigated by SEM (JEOL JSM-7800F, 5 kV). Further imaging and SAED were performed by TEM (JEOL 2100F, 200 kV and FEI Titan G2 60-300, 300 kV). Elemental mappings were collected using the FEI microscope equipped with an EDS (super-EDS) system. The Seebeck coefficient and electrical conductivity of sintered pellets were measured simultaneously using a Linseis LSR-3 instrument from 310 to 710 K. The thermal conductivity (κ) was calculated using $\kappa = DC\rho$, where thermal diffusivity (D) was measured using a Netzsch LFA-457 instrument from 300 to 710 K, specific heat capacity ($C_p$) was measured using a differential scanning calorimeter (Netzsch, 404F3), and sample density (p) was measured using Archimedes’ method. Hall measurements were performed on a home-made apparatus under a reversible magnetic field of 1.0 T.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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