Nanobulk Thermoelectric Materials Fabricated from Chemically Synthesized Cu$_3$Zn$_{1-x}$Al$_x$Sn$_{5-y}$ Nanocrystals

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Supporting Information

ABSTRACT: Direct energy conversion of heat into electricity using thermoelectric materials is an attractive solution to help address global energy issues. Developing novel materials composed of earth-abundant and nontoxic elements will aid progress toward the goal of sustainable thermoelectric materials. In this study, we chemically synthesized Cu−Zn−Sn−S nanocrystals and fabricated a Cu$_3$ZnSnS$_5$ thermoelectric material using nanocrystals as building blocks. The figure-of-merit (ZT) value of the Cu$_3$ZnSnS$_5$ nanocrystals was found to be 0.39 at 658 K. We substituted Zn with Al in the Cu$_3$ZnSnS$_5$ system to form Cu$_3$Zn$_{1-x}$Al$_x$Sn$_{5-y}$ (x = 0.25, 0.5, 0.75, and 1) to lower the lattice thermal conductivity of the resulting materials. Complete substitution of Al for Zn substantially decreased the lattice thermal conductivity and dramatically increased the electrical conductivity of the material. However, the ZT value could not be significantly enhanced, which could be primarily attributed to the high carrier thermal conductivity. These results highlight the production of Cu$_3$Zn$_{1-x}$Al$_x$Sn$_{5-y}$ thermoelectric materials and unveil the scope for improvement of ZT values by altering transport properties.

INTRODUCTION

Waste heat recovery has attracted attention in the last few decades, which has led to rapid progress in the development of thermoelectric materials. The performance of thermoelectric materials can be rated through a dimensionless quantity called the figure of merit (ZT), which is expressed as

$$ZT = \frac{\sigma S^2 T}{\kappa}$$

where $\sigma$, $S$, $\kappa$, and $T$ are electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature, respectively. To improve the ZT value, it is important to increase the power factor (PF = $\sigma S^2$) and/or decrease $\kappa$. In nanostructured materials, $\kappa$ can be decreased considerably by lowering the lattice thermal conductivity ($\kappa_{lat}$) through phonon scattering at grain boundaries,$^{1,2}$ whereas PF can be enhanced through quantum confinement or energy filtering. Several researchers have demonstrated the enhancement of ZT through nanostructuring, such as the formation of sintered nanocomposites.$^{4,5}$ However, most of these materials are prepared through complicated processes that are both energy- and time-consuming, which limit the development of thermoelectric materials and the wide application of thermoelectric devices. Furthermore, most thermoelectric materials are composed of heavy transition metals or rare earth elements, such as Sb or Te.$^6$ The exploitation of rare natural reserves makes such technology unsustainable. Therefore, it remains important to develop versatile thermoelectric materials from earth-abundant and eco-friendly constituent elements using scalable nanoparticle synthesis techniques and subsequent processing into bulk structures using facile methodologies.

Materials scientists have been exploring a wide range of cost-effective and eco-friendly materials that can be used in thermoelectric applications. Quaternary semiconductor copper zinc tin sulfide (Cu$_2$ZnSnS$_4$ CZTS) is one such material that has been widely explored for use in solar cells and has the ability to behave as a thermoelectric material because of its low $\kappa$ and high $S$. Undoped CZTS achieved a ZT value of 0.026 at 700 K.$^8$ Interestingly, Cu-doped CZTS (Cu$_{2+2x}$Zn$_{0.80}$Sn$_{0.75}$S$_{3.53}$) exhibited a ZT value of 0.14 at 700 K, which is 5 times higher than that of stoichiometric CZTS, even though this ZT value is still low.$^8$ The low ZT value of CZTS is mainly caused by its low $\sigma$.$^7$ To improve the thermoelectric properties of CZTS, Zn

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atoms have been substituted with other transition-metal atoms and/or S atoms have been substituted with Se atoms using various techniques including solid-state reaction, mechanical alloying, and wet chemical synthesis. The results obtained by such modifications of CZTS are promising, for example, $ZT = 0.86$ (at 800 K) for Cu$_2$Zn$_{0.9}$SnSe$_{4.16}$, $ZT = 0.7$ (at 850 K) for Cu$_2$CoSnSe$_{4}$ at 850 K, $ZT = 0.71$ (at 685 K) for Cu$_{2.11}$Cd$_{0.89}$SnSe$_{3.9}$ at 685 K, and $ZT = 0.6$ (at 800 K) for Cu$_{1.9}$Mn$_{0.9}$SnSe$_{4.16}$. In addition, by replacing S with Se and Sn with Ge, the $ZT$ value has also been markedly enhanced. For instance, $ZT = 0.55$ (at 723 K) for Cu$_{2.17}$Zn$_{0.85}$GeSe$_{4.18}$ and $ZT = 0.45$ (at 670 K) for Cu$_{0.75}$Zn$_{0.25}$GeSe$_{4.18}$. However, these materials are no longer CZTS, and most of them contain rarer and more toxic elements than CZTS.

Recently, we reported that the $ZT$ value of Zn-doped Cu$_2$SnS$_3$ (Cu$_2$Sn$_{1−x}$Zn$_x$S)$_{3}$ could be dramatically enhanced up to 0.64 (at 670 K) by multiscale defect engineering. This result suggests that the thermoelectric performance of existing systems can be substantially improved by controlling atomic structural properties such as lattice defects and nonstoichiometry along with impurities, nanostructure, and mesoscale structure. Therefore, multiscale defect engineering represents a new possibility to improve the $ZT$ values of materials composed of sustainable elements with inferior thermoelectric performance.

Pan and co-workers synthesized wurtzite Cu$_3$InSnS$_5$ (CITS) nanocrystals, which belong to the I$_{3−IV}$−VI$_1$ family (a new generation of copper-based quaternary semiconductor), for solar cell applications. However, the scarcity of In will limit the practical use of CITS materials. Bai et al. recently reported that Cu$_3$AlSnS$_5$ (CATS) is a sustainable I$_{3−IV}$−VI$_1$ semiconductor that may be suitable as an alternative to CITS. In a nod to the materials described above, in this study, we attempt to synthesize Cu$_{3−x}$Zn$_x$Al$_{1−x}$Sn$_{3−y}$S$_{5−y}$ nanocrystals as building blocks for sustainable thermoelectric materials by revisiting materials based on Cu, Zn, Sn, and S. Note that Cu$_{3}$Zn$_{3}$Sn$_{3}$S$_{5}$ differs from conventional CZTS. The reason why Al is incorporated into Cu−Zn−Sn−S nanocrystals is that ab initio calculations predicted that the incorporation of Al into the I$_{3−IV}$−VI$_1$ system may cause $κ_{\text{lat}}$ to decrease.

## RESULTS AND DISCUSSION

**Morphology and Crystal Structure of Nanocrystals.**

Cu$_{3−x}$Zn$_x$Al$_{1−x}$Sn$_{3−y}$S$_{5−y}$ ($x = 0−1$) nanocrystals with five different compositions were synthesized, which are referred to as Powder$_0$, Powder$_{0.25}$, Powder$_{0.5}$, Powder$_{0.75}$, and Powder$_1$ corresponding to $x = 0, 0.25, 0.5, 0.75,$ and 1, respectively. Depending on $x$, $y$ could vary to maintain electroneutrality of the system. Transmission electron microscopy (TEM) images of the as-synthesized nanocrystals are shown in Figure 1. All nanocrystals were uniform in size and shape with a hexagonal pencil-like morphology (several nanocrystals are standing up and others are lying down on the TEM grid). Average lengths and widths of nanocrystals are shown in Figure 1f, which indicates that the nanocrystal size decreases with increasing Al content. Because the nanocrystal size fundamentally depends on nucleation and growth as well as adsorption/desorption processes, one plausible reason for the decrease in nanocrystal size with increasing $x$ is the low affinity between Al and 1-dodecanethiol (DTT) compared to that between Zn and DTT. This phenomenon can be explained by the hard/soft-acid/base principle. Namely, the sulfide (DDT) is a soft base and Cu, Zn, and Al are soft, moderate, and hard acids, respectively.

The Cu/Zn/Al/Sn atomic ratios for Powder$_0$, Powder$_{0.25}$, Powder$_{0.5}$, Powder$_{0.75}$, and Powder$_1$ were determined to be 59:22:0:19, 57:17:6:20, 63:5:14:18, and 63:0:19:18, respectively, by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) analysis, which are approximately equal to the nominal compositions of Cu$_{3−x}$Zn$_x$Al$_{1−x}$Sn$_{3−y}$S$_{5−y}$ with $x = 0, 0.25, 0.5, 0.75,$ and 1, respectively. To determine the oxidation states of elements in the nanocrystals, core-level X-ray photoelectron spectroscopy (XPS) analysis of Powder$_1$ was performed. Figure S1 shows Cu 2p, Al 2p, Sn 3d, and S 2p spectra obtained for this sample. The binding energies of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ were 932.2 and 952.1 eV, respectively. The peak separation of 19.9 eV is indicative of the presence of Cu$. The peak from Al 2p$_{3/2}$ appeared at the binding energy of 74.6 eV, which was assigned to Al$^3+$. The presence of Sn$^{4+}$ was confirmed by the observation of peaks at 486.4 eV (3d$_{5/2}$) and 494.8 eV (3d$_{3/2}$) with a characteristic peak separation of 8.4 eV. The presence of S$^{2−}$ was confirmed by the peaks located at 161.5 eV (2p$_{3/2}$) and 162.6 eV (2p$_{1/2}$) with a peak splitting of 1.1 eV, which was consistent with the literature value for metal sulfides.

Figure 2 shows the X-ray diffraction (XRD) patterns of Powder$_0$, Powder$_{0.25}$, and Powder$_1$. The XRD patterns of Powder$_{0.25}$ and Powder$_{0.75}$ are provided in Figure S2. Rietveld refinement of the XRD patterns was performed with the FullProf program using wurtzite (WZ) and zinc blende (ZB) ZnS crystallographic information files. Simulated patterns in which Cu, Sn, and Al ions randomly substitute Zn sites in the ZnS structure are shown as black lines, and occupancy parameters are listed in Table S1. The crystal structures of Powder$_0$, Powder$_{0.25}$, Powder$_{0.5}$, Powder$_{0.75}$, and Powder$_1$ are presented in Figure S3.

Rietveld refinement revealed that the primary crystal structure of all nanocrystals was WZ with small amounts of ZB (Table S2). The fraction of ZB probably varied because the difference in the oxidation states of Zn$^{2+}$ and Al$^{3+}$ altered the degree of electrostatic interactions in the samples, yielding different crystal structures. The mean crystalline size ($D_{\text{cal}}$) was calculated with the Scherrer equation using the primary peak of the WZ phase. $D_{\text{cal}}$ values calculated for Powder$_0$, Powder$_{0.25}$, Powder$_{0.5}$, Powder$_{0.75}$, and Powder$_1$
patterns. Cu₃AlSnS₅ nanocrystals as shown in Figure S4. The Bragg reflection positions are shown as short green bars below the diffraction patterns. The blue lines represent difference patterns.

Figure 2. Rietveld refinement of powder XRD patterns of (a) Powder_0, (b) Powder_0.5, and (c) Powder_1. The experimental patterns are shown as red lines, and the calculated patterns are shown as black lines. The Bragg reflection positions are shown as short green bars below the diffraction patterns. The blue lines represent difference patterns.

planes of WZ were clearly seen in all cases. To confirm that all elements are within each nanocrystal, EDS elemental mapping was carried out for CuₓZnₙ₋ₓAlₙSnₙSnₙ₋ₙ with x = 0, 0.25, 0.5, 0.75, and 1, respectively. The measured densities of Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1 were 4.522, 4.531, 4.518, 4.544, and 4.356 g·cm⁻³, respectively. Thus, the relative densities of all pellets were higher than 95%.

Figure 4a–e shows XRD patterns of the pellets. To perform quantitative phase-composition analysis of the pellets, Rietveld refinement of their XRD patterns was performed. Figure 4f shows the weight percentage of the WZ phase in each pellet. A phase transition from WZ to ZB was clearly observed for all pellets during sintering. Specifically, Pellet_0 consisted of a pure ZB phase after sintering. The phase transition was ascribed to the greater thermodynamic stability of the ZB phase than that of the WZ phase because of the more symmetrical structure of the former, which might increase with the Zn content and thereby facilitate the phase transition. The lattice constants of the ZB phase are plotted as a function of x in Figure S5. The calculated Dₐₜ values of Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1 were 22.7, 20.2, 21.5, 17.7, and 19.8 nm, respectively, indicating that Dₐₜ slightly increased during sintering for all the pellets.

Crystal Structure of Pellets. Pellets were fabricated from the powder samples. The pellets fabricated from Powder_0, Powder_0.25, Powder_0.5, Powder_0.75, and Powder_1 are referred to as Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1, respectively. The measured Cu/Zn/Al/Sn atomic ratios for Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1 were 59:21:0:20, 58:17:7:18, 61:9:9:21, 60:6:16:18, and 61:0:22:17, respectively, which were approximately equal to the nominal compositions of Cu₁₋ₓZnₓ₋ₓAlₓSnₓSn₉₋ₓ with x = 0, 0.25, 0.5, 0.75, and 1, respectively. The measured densities of Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1 were 4.522, 4.531, 4.518, 4.544, and 4.356 g·cm⁻³, respectively. Thus, the relative densities of all pellets were higher than 95%.

Figure 3. HAADF-STEM images of single CuₓZn₁₋ₓAlₓSnₓSn₉₋ₓ nanocrystals as shown in Figure S4.

Figure 3. HAADF-STEM images of single CuₓZn₁₋ₓAlₓSnₓSn₉₋ₓ nanocrystals with x = (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1. The lattice fringes with an interplanar spacing of 0.33–0.38 nm are ascribed to the {100} planes of WZ.

Crystal Structure of Pellets. Pellets were fabricated from the powder samples. The pellets fabricated from Powder_0, Powder_0.25, Powder_0.5, Powder_0.75, and Powder_1 are referred to as Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1, respectively. The measured Cu/Zn/Al/Sn atomic ratios for Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1 were 59:21:0:20, 58:17:7:18, 61:9:9:21, 60:6:16:18, and 61:0:22:17, respectively, which were approximately equal to the nominal compositions of Cu₁₋ₓZnₓ₋ₓAlₓSnₓSn₉₋ₓ with x = 0, 0.25, 0.5, 0.75, and 1, respectively. The measured densities of Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1 were 4.522, 4.531, 4.518, 4.544, and 4.356 g·cm⁻³, respectively. Thus, the relative densities of all pellets were higher than 95%.

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Thermoelectric Properties. Figure 5 shows the thermoelectric properties of Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1. Thermal diffusivities and specific heats for all pellets are provided in Figure S6. As shown in Figure 5a, σ decreases with temperature, indicating the metallic behavior of the pellets. It is noteworthy that the σ values of Pellet_1 are an order of magnitude higher than those of the other pellets as well as those of other high-performance copper sulfide-based thermoelectric materials including Cu₁₋ₓSnₓ, Cu₁₀Ni₂Sb₄S₁₃, and Cu₂₀V₂Sn₆S₃₂. It is interesting to compare the thermoelectric properties of our samples with those of reported CZTS materials (Figure S7). Cu-doped CZTS (Cu₂₋ₓZn₀₋ₓSn₀₋ₓS₁₋ₓ) exhibited a σ value that was 38 times higher than that of undoped CZTS at 700 K (Figure S7a). The atomic fraction of Cu in our pellet
samples was higher than that in Cu-doped CZTS, and the σ values of our pellets were much higher than that of Cu-doped CZTS, as shown in Figure S7a.

Figure 5b illustrates the temperature dependence of S. In general, S depends inversely on σ. However, the S values of Pellet_0, Pellet_0.25, Pellet_0.5, and Pellet_0.75 are approximately the same as that of Cu-doped CZTS (Figure S7b), even though the σ values of these pellets are much higher than that of Cu-doped CZTS, resulting in our pellets displaying much higher PF values than those of CZTS materials. Though it is not appropriate to directly compare the electrical transport properties of the CuZn1−xAlxSnS3−y materials, which are I−II/III−IV−VI2 semiconductors with the ZB structure, with those of conventional CZTS materials, which are I−II−IV−VI2 semiconductors with the tetragonal crystal structure, we would like to emphasize that the electrical transport properties of CuZn1−xAlxSnS3−y materials differ markedly from those of CZTS materials. It should be noted that we measured S and σ in both heating and cooling cycles and found that the values coincided in both types of cycles (Figure S8).

Figure 5c displays the temperature dependence of κ. The κ values are quite low for all pellets except for Pellet_1, and κ shows almost no temperature dependence. This is more evident in Figure S7c,d, where κlat of undoped CZTS exhibits the classical 1/T dependence caused by the Umklapp scattering, whereas the characteristic 1/T dependence of κlat completely disappeared for the CuZn1−xAlxSnS3−y materials, indicating that the phonon scattering is dominated by defect scattering including nanograins and lattice distortion. In addition, the κlat values decreased with increasing x, as expected. The reason for the disappearance of the 1/T dependence of κlat in the case of Cu-doped CZTS has been explained by lattice distortion generated by excess Cu dopants occupying Zn positions in the lattice.8

Figure 5e,f shows the temperature dependences of PF and ZT values, respectively. Pellet_0 and Pellet_0.5 exhibited ZT values of 0.39 (at 658 K) and 0.40 (at 666 K), respectively; these values are approximately 15 and 3 times higher than the ZT values (at 700 K) of undoped and Cu-doped CZTS materials8 respectively. The ZT value of Pellet_1 was only 0.12 (at 668 K), which was mainly due to Pellet_1 having a high σ, resulting in the high carrier thermal conductivity (κlat) (Figure S9). Therefore, there is a high possibility of improvement of the ZT value of CATS materials by lowering σ to decrease κlat because κlat of CATS is already quite low (∼0.3 W m−1 K−1), as shown in Figure 5d. The decrease of σ can be achieved in several ways; for example, incorporating nanoenclosures in the material to scatter carriers or decreasing the size of nanocrystals.

Pellet_0 (Cu3ZnSnS5) consisted of a pure ZB phase accompanied with high S compared to those of metals and high σ compared to those of intrinsic semiconductors, implying that Pellet_0 is a degenerate semiconductor. In contrast, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1 consisted of mixtures of ZB and WZ phases. The weight percentage of the WZ phase increased with the Al content, as shown in Figure 4f. The S and σ values of the pellets at 375 and 650 K are summarized in Table S3 as well as the weight percentages of ZB and WZ phases of all pellets. Both S and σ exhibited complex behavior with respect to x, indicating that the fraction of the ZB phase has a noticeable effect on the electrical transport properties of the pellets. Even though the amount of data was insufficient, one could argue that the carrier concentration of CuZn1−xAlxSnS3−y materials seems to increase with the Al content if one compares the characteristics of Pellet_0.25 and Pellet_0.5 or Pellet_0.75 and Pellet_1, which have similar weight percentages of the ZB phase (Table S3). To confirm this hypothesis, based on the free electron model, Fermi energy EF can be described as

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

(1)

where h is the Dirac constant, $k_F = (3\pi^2 n)^{1/3}$ is the wavenumber at the Fermi surface, and n is the carrier concentration. We assumed that an acoustic phonon scattering of carriers is dominant at the high-temperature region. According to this assumption, S can be described as below

$$\sigma = A e^{\frac{\varepsilon}{T}}$$

(2)

$$S = -\frac{\pi^2 k_B^2 T}{3e} \left| \frac{\partial \ln \sigma}{\partial \varepsilon} \right|_{\varepsilon = E_F} = \frac{\pi^2 k_B^2 T}{6eE_F}$$

(3)

where A is the arbitrary constant, $\varepsilon$ is the energy, $\gamma$ is the scattering parameter, $k_B$ is the Boltzmann constant, and $\varepsilon$ is the elementary charge. When the carrier scattering is dominated by acoustic phonon scattering, $\gamma = -1/2$. From eqs 1–3, the values of n and mobility (μ) were estimated as shown in Table S4. The value of μ is low for all pellets as compared to typical semiconductors probably because of the defect scattering.
These results create opportunity for finer tuning of the material physical properties contributing toward better understanding of their thermoelectric performances.

**CONCLUSIONS**

A novel series of thermoelectric materials was chemically synthesized with earth-abundant and eco-friendly elements. Incorporation of Al in the Cu–Zn–Sn–S system decreased $k_{\text{tot}}$ by about 4 times and enhanced $\sigma$ by an order of magnitude at most. In consequence, Cu$_x$Zn$_{1-x}$Al$_x$SnS$_{5-y}$ (x = 0 and 0.5) materials exhibited ZT values of 0.39 (at 658 K) and 0.40 (at 666 K), respectively, which are approximately 15 times higher than that of conventional CZTS. It was challenging to determine the most important factor to control the ZT value because incorporation of Al changed not only the material stoichiometry but also the phase fraction and crystal structure and their dependent parameters. This research contributes to the development of Cu–Zn/Al–Sn–S-based semiconductors as sustainable thermoelectric materials and creates space for further development of a profound understanding of transport properties and ZT values without sacrificing sustainability.

**EXPERIMENTAL SECTION**

**Synthesis of Cu$_x$Zn$_{1-x}$Al$_x$SnS$_{5-y}$ Nanocrystals.** DDT (purity 99%), oleylamine (OAM, purity 70%), copper(II) acetylacetonate [Cu(acac)$_2$, purity 98%], zinc(II) acetylacetonate hydrate [Zn(acac)$_2$, purity 99.995%], and tin(II) acetate [Sn(OAc)$_2$] were purchased from Sigma-Aldrich, Japan. All chemicals were used without any further purification.

Cu$_x$Zn$_{1-x}$SnS$_{5-y}$ nanocrystals were synthesized as follows. Cu(acac)$_2$ (5 mmol), Sn(OAc)$_2$ (2 mmol), Zn(acac)$_2$ (1 mmol), and DDT (100 mL) were added to a three-necked flask equipped with a dry Ar inlet/outlet, trap sphere, condenser, heating mantle, thermocouple, and magnetic stirrer. First, the reaction mixture was stirred with Ar bubbling at room temperature for 5 min. Then, the temperature was increased to 100 °C and kept there for 10 min with Ar bubbling to remove volatile matter. Subsequently, the reaction temperature was further raised to 260 °C and held there for 1 h. After cooling the reaction mixture, the nanocrystals were separated from the reaction mixture by centrifugation at 5000 rpm for 3 min. The nanocrystals were then washed three times by repeating the following purification cycle: redispersion in hexane, centrifugation, and supernatant decantation. Finally, the obtained nanocrystals were dried under vacuum. Cu$_x$Zn$_{1-x}$Al$_x$SnS$_{5-y}$ nanocrystals were also synthesized in a similar manner by varying the input molar ratio of aluminum acetylacetonate [Al(acac)$_3$, purity 99%] (x) to Zn(acac)$_2$ while keeping the total amount of those two precursors constant [Al(acac)$_3$ + Zn(acac)$_2$ = 1 mmol].

**Ligand Exchange.** Thiourea (TU; Tokyo Chemical Industry, 10 g) was dissolved in methanol (Kanto Chemical, 400 mL). The TU solution was added to a dispersion of the nanocrystals (3.4 g) in toluene (250 mL). The mixture was sonicated for 1 h at room temperature. After the ligand exchange reaction, TU-capped nanocrystals were separated from the solution by centrifugation at 5000 rpm for 3 min. The TU-capped nanocrystals were washed by redispersion in a hexane/toluene mixture, centrifugation, and supernatant decantation. The TU-capped nanocrystals were redispersed in methanol (400 mL), and then toluene (125 mL) was added. The dispersion was subjected to centrifugation at 5000 rpm for 10 min to remove excess TU.

**Pelletization.** After ligand exchange, nanocrystals were pelletized into a solid disk with a diameter of 10 mm and a thickness of 2–3 mm using a pulsed electric current sintering machine (Sinterland LABOX-100) under the following conditions: vacuum, 3.5 Pa; temperature, 450 °C; pelletization pressure, 30 MPa; and sintering time, 5 min. The pellets fabricated from Powder_0, Powder_0.25, Powder_0.5, Powder_0.75, and Powder_1 are referred to as Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1, respectively. The pellets were polished using silicon carbide abrasive paper (grit size 2000) before characterization. The densities of pellets were determined using a gas pycnometer (Shimadzu AccuPyc II 1340).

**Structural and Compositional Analyses.** The synthesized nanocrystals were characterized by TEM (Hitachi H-7650 operated at 100 kV), XRD using a Rigaku SmartLab diffractometer with Cu Kα radiation, STEM equipped with a HAADF detector and an EDS system (JEOL JEM-ARM200F operated at 200 kV), SEM (Hitachi TM3030) equipped with an EDS system, and XPS (Shimadzu Kratos AXIS-ULTRA DLD). The pellets were characterized by XRD and SEM/EDS.

**Measurement of Thermoelectric Properties.** First, $\kappa$ was measured for the pellets in the cross-plane direction by laser flash analysis (Netzsch LFA447). In this method, $\kappa$ (W m$^{-1}$ K$^{-1}$) was calculated as $\kappa = \frac{dC}{dT}$, where $d$ (kg m$^{-3}$), $c$ (J kg$^{-1}$ K$^{-1}$), and $D$ (m$^2$ s$^{-1}$) are the density, specific heat, and thermal diffusivity of the pellet, respectively. Then, $S$ and electrical resistivity ($\rho$) were measured in the in-plane direction by a ZEM-3 analyzer (ULVAC-Riko). The carrier thermal conductivity, $\kappa_{\text{car}}$, was calculated as $\kappa_{\text{car}} = \frac{L}{\rho T} = \frac{PT}{L}$, where $L$ denotes the Lorenz number (2.44 × 10$^{-8}$ W Ω K$^{-2}$). Then, $\kappa_{\text{tot}}$ was calculated as $\kappa_{\text{tot}} = \kappa - \kappa_{\text{car}}$. The ZT value was calculated as $ZT = \frac{\sigma S^2 T}{\kappa}$.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01944.

XPS profile of Powder_1; XRD patterns of Powder_0.25 and Powder_0.75; crystal structures of Cu$_x$Zn$_{1-x}$Al$_x$SnS$_{5-y}$ samples and the occupancy parameter of each atom; WZ and ZB contents of Cu$_x$Zn$_{1-x}$Al$_x$SnS$_{5-y}$ nanocrystals; EDS elemental mapping images of Cu$_x$Zn$_{1-x}$SnS$_{5-y}$, Cu$_x$Zn$_{0.5}$Al$_{0.5}$SnS$_{4.5}$, and Cu$_x$AlSnS$_{3}$ nanocrystals; lattice parameter of ZB as a function of x for Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1; thermal diffusivities and specific heats for Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1; $\sigma$, $S$, $\kappa$, $\kappa_{\text{tot}}$, PF, and ZT values of Powder_0, Powder_0.25, Powder_0.5, Powder_0.75, and Pellet_1 compared with Cu-doped CZTS (Cu$_{2.79}$Zn$_{0.20}$Sn$_{0.73}$S$_{5.53}$), and undoped CZTS materials; values of $\sigma$ and $S$ measured in both heating and cooling cycles for Pellet_0, Pellet_0.25, Pellet_0.5, Pellet_0.75, and Pellet_1; $\sigma$ and $S$ values at 375 and 650 K and the weight percentages of ZB and WZ phases of all pellets; and estimated values of $n$ and $\mu$ at 375 K of all pellets (PDF).
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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