Enhancing thermoelectric performance of (Cu$_{1-x}$Ag$_x$)$_2$Se via CuAgSe secondary phase and porous design

Weidi Liu a, Xiaolei Shi a, Raza Moshwana, Min Hongb, a, Lei Yangc, Zhi-Gang Chenb, a, Jin Zoua, d, **

a Materials Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia
b Centre for Future Materials, University of Southern Queensland, Springfield, Queensland 4300, Australia
c School of Materials Science and Engineering, Sichuan University, Chengdu 610065, China
d Centre for Microscopy and Microanalysis, The University of Queensland, Brisbane, Queensland 4072, Australia

Abstract

In the field of thermoelectrics, Cu$_2$Se has attracted extensive attention due to its ultralow lattice thermal conductivity ($\kappa_l$) deriving from its superionicity. Here, we develop a solvothermal method to synthesize Ag-alloyed Cu$_2$Se powders, subsequently sintered to form porous pellets by spark plasma sintering. After detailed characterization, we found that CuAgSe secondary phase forms when Ag has easily surpassed its solubility limit of ~1 at. % and the chemical reaction during the spark plasma sintering causes the formations of the porous structure. Benefiting from these structural features, a very low $\kappa_l$ of ~0.23 W m$^{-1}$ K$^{-1}$ and in turn an improved figure of merit of ~1.1 at 773 K were secured in the (Cu$_{0.93}$Ag$_{0.07}$)$_2$Se pellet. This study suggests that the thermoelectric performance of Cu$_2$Se can be further enhanced by reducing $\kappa_l$ via effective engineering methods, such as porosity engineering and introducing additional secondary phase.

Keywords:
Thermoelectric performance
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Porous
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1. Introduction

Thermoelectric materials, which can realize direct conversion between heat and electricity, have attracted extensive attention in the past decades [1, 2]. The efficiency of thermoelectric materials is evaluated via the dimensionless figure of merit ($zT$) expressed as $zT = S^2\sigma T/(\kappa_l + \kappa_{\text{el}})$, where $S$, $\sigma$, $T$, $\kappa_l$, and $\kappa_{\text{el}}$ are the Seebeck coefficient, electrical conductivity, absolute temperature, electrical thermal conductivity, and lattice thermal conductivity, respectively [3, 4]. In addition, $S\sigma$ is defined as the power factor to evaluate the electrical performance. Recently, new high-performance thermoelectric materials have been brought into sight with several novel concepts, including phonon-glass electron-crystal (PGEc) [5, 6], hierarchical architecture engineering [7], quantum confinement [8, 9], and band engineering [10]. Among them, PGEc [5, 6], which combines the high electronic conductivity of a crystal with the low thermal conduction of a glass, has been used to optimise $zT$ of clathrates [11] and skutterudites [12].

An extension of PGEc, the phonon-liquid electron-crystal (PLEc) concept has also been proposed in Cu$_2$Se material system [1]. Typically, superionic Cu$_2$Se has an anti-fluorite crystal structure [1]. After phase transition from $\alpha$-Cu$_2$Se to $\beta$-Cu$_2$Se at ~400 K [13], the high-temperature $\beta$-Cu$_2$Se may be simplified into Cu sublattice diffusing around crystalline Se sublattice, where the diffusion coefficient of Cu in $\beta$-Cu$_2$Se is in the same order of magnitude of water ($~10^{-5}$ cm$^2$ s$^{-1}$) [14]. Liquid-like behaviour of Cu sublattice in $\beta$-Cu$_2$Se not only help scatter phonons to approach the glass-limit of $\kappa_l$, but also break through this limit by further eliminating some shear vibrational modes [1]. Deriving from the PLEC concept, $\kappa_l$ of bulk $\beta$-Cu$_2$Se can be as low as 0.5 W m$^{-1}$ K$^{-1}$ at ~1000 K, leading to a peak $zT$ as high as 1.5 [1].

Although $\kappa_l$ of $\beta$-Cu$_2$Se is already low, it may be further reduced to enhance $zT$ values of Cu$_2$Se [15]. For example, with $\kappa_l$ as low as ~0.3 W m$^{-1}$ K$^{-1}$, peak $zT$ of Cu$_2$Se$_{0.92}$S$_{0.08}$ can reach ~2.0 at 1000 K [16]. Furthermore, with nearly negligible $\kappa_l$ peak $zT$ of In-doped (Cu$_2$Se)$_{0.95}$CuInSe$_{0.05}$ has reached ~2.6 at ~850 K [17]. In fact, $\kappa_l$ of $\beta$-Cu$_2$Se has been reduced by element-doping [18], especially heavy elements, which introduces large mass and radius fluctuations [18, 19]. Besides, introducing additional secondary phases can also significantly reduce $\kappa_l$ in $\beta$-Cu$_2$Se, such as using carbon-based materials to form secondary phases [20, 21].

Low $\kappa_l$ of $\beta$-Cu$_2$Se, originating from liquid-like behaviour of Cu sublattice, is also strongly related with the ionic diffusion coefficient or ionic conductivity [14]. Higher ionic conductivity indicating potentially higher level of atomic disorder and lower $\kappa_l$ has been observed in Ag-alloyed Cu$_2$Se comparing with pristine Cu$_2$Se [22]. This indicates that Ag-alloying may lower $\kappa_l$ to enhance $zT$ in impurity-alloyed Cu$_2$Se.
In this study, (Cu_{1-x}Ag_x)2Se powders were synthesized by a facile solvothermal method, which were subsequently sintered to form porous pellets by spark plasma sintering (SPS). An ultralow $\kappa_l$ of ~0.23 W m$^{-1}$ K$^{-1}$ and enhanced peak $zT$ of ~1.1 at 773 K were observed in porous (Cu_{1-x}Ag_x)2Se pellets. Through detailed microscope characterization, we clarify the underlying mechanism.

2. Experiment

2.1. Solvothermal synthesis of (Cu_{1-x}Ag_x)2Se powders

The (Cu_{1-x}Ag_x)2Se powders were synthesized via a facile solvothermal method by employing CuO (98%), Na$_2$SeO$_3$ (99%), Ag$_2$O (99%), NaOH (97%), ethylene glycol (99.8%) and polyvinylpyrrolidone (PVP, average molecular weight 40,000) as precursors (purchased from Sigma Aldrich). In a typical solvothermal synthesis process, 0.4000 g PVP was dissolved in 36 mL ethylene glycol by continuous stirring for ~1 min under a stirring speed of ~500 r·min$^{-1}$ in a 125 mL Teflon container. Then, 4.0 mL NaOH solution (10 mol·L$^{-1}$) and 1.7294 g Na$_2$SeO$_3$ were in turn added into the solvent. Following this was adding varying amounts of Ag$_2$O and CuO for x = 0, 0.01, 0.03 and 0.07 of (Cu$_{1-x}$Ag$_x$)2Se powders. The Teflon containers containing all precursors were then sealed in stainless steel autoclaves, heated to 230 °C under a heating rate of 200 °C·h$^{-1}$, dwelled for 24 h in a CSK thermal oven. After that, the containers were slowly cooled to room-temperature during 24 h. The obtained powders were collected by centrifuging and

Fig. 1. Temperature (T)-dependent thermoelectric performance of the as-sintered porous (Cu$_{1-x}$Ag$_x$)2Se pellets (x = 0.01, 0.03 and 0.07): (a) electrical conductivity ($\sigma$), (b) Seebeck coefficient ($S$), (c) power factor ($S^2\sigma$), (d) total thermal conductivity ($\kappa$), (e) lattice thermal conductivity ($\kappa_l$) and (f) dimensionless figure of merit ($zT$).
washed by absolute ethanol and deionized water several times. Finally, the synthesized powders were dried under 60 °C for at least 12 h.

2.2. Spark plasma sintering to form (Cu1-xAgx)2Se pellets

For thermoelectric performance measurements, synthesized (Cu1-xAgx)2Se powders were sintered into pellets by SPS. Each pellet was sintered from 1.40 g powders. During a typical sintering process, the powders were firstly cold-pressed under 50 MPa for 5 min in SPS, then directly heated up to 500 °C in 4 min and dwelled for 5 min under vacuum. After sintering, the sintered pellets were naturally cooled to room-temperature.

2.3. Thermoelectric performance measurement of (Cu1-xAgx)2Se pellets

Total thermal conductivity (κ) of (Cu1-xAgx)2Se pellets were calculated by

\[ \kappa = \rho \cdot C_p \cdot D, \]

where \( \rho \), \( C_p \) and \( D \) are the density, specific heat capacity, and thermal diffusivity, respectively. \( \rho \) measured by the Archimedes method was between 5.50 g cm\(^{-3}\) and 6.00 g cm\(^{-3}\) (82–91% of the theoretical ones). \( C_p \) was measured by DSC 404 F3 (NETZSCH) and \( D \) was measured by LFA 457 (NETZSCH). \( \kappa_e \) was estimated by subtracting \( \kappa_e = L \cdot \sigma \cdot T \), where \( L \) is the Lorenz factor [23]. Here, the \( L \) was calculated based on single parabolic band model [24–26]. \( \sigma \) and \( S \) were measured simultaneously by ZEM-3 (ULVAC). The carrier concentration (\( n_H \)) was measured by the van der Pauw technique under a reversible magnetic field of ±1.5 T. The carrier mobility (\( \mu_H \)) was evaluated based on measured \( \sigma \) and \( n_H \) using the relationship of \( \sigma = n_H e \cdot \mu_H \). The uncertainty (measurement errors) of \( S \), \( \sigma \), \( D \) and \( C_p \) measurements were established as 5%, which cause the measurement uncertainty for \( S^2 \sigma \) and \( zT \) as 10% and 12%, respectively. The uncertainty of \( n_H \) and \( \mu_H \) were acquired from fluctuation of the repeatedly measured data.

2.4. Structural characterization of (Cu1-xAgx)2Se powders and pellets

The crystal structures and phases of both (Cu1-xAgx)2Se synthesized powders and sintered pellets were characterized by X-ray diffraction (XRD) recorded by a Bruker D8 advanced powder XRD equipment with a graphite monochromatized Cu Kα radiation (\( \lambda = 0.15408 \) nm). Rietveld refinement (MAUD) was carried out for phase content analysis and lattice parameter calculation. The Ag-content (x) of sintered (Cu1-xAgx)2Se pellets were measured by X-ray energy dispersive spectroscopy (EDS) microanalysis equipped on a scanning electron microscope (SEM, JEOL JSM-7100F). To statistically determine composition, we have randomly analysed 3–5 areas in each pellet. In each area, we have randomly analysed 3–5 points.

3. Results and discussion

3.1. The influence of additional CuAgSe secondary phase on thermoelectric performance of (Cu1-xAgx)2Se

Fig. 1 shows the temperature-dependent \( \sigma \), \( S \), \( S^2 \sigma \), \( \kappa \), \( \kappa_e \), and \( zT \) of the sintered (Cu1-xAgx)2Se (x = 0.01, 0.03 and 0.07) pellets. Here, we focus on the thermoelectric performance at the temperature \( T > 400 \) K. For x > 0.01, with increasing x, \( \sigma \) at 773 K (Fig. 1a) has reduced ~46% from 133 S cm\(^{-1}\) of (Cu0.99Ag0.01)2Se to 91 S cm\(^{-1}\) of (Cu0.93Ag0.07)2Se. \( S \) at 773 K (Fig. 1b) only increased slightly. Dominated by the reduction of

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**Fig. 2.** (a) XRD patterns of sintered (Cu1-xAgx)2Se pellets (x = 0.01, 0.03 and 0.07), (b) enlarged 071 and 090 peaks of CuSe, (c) enlarged 002 and 150 peaks of CuAgSe, (d) BSE image and corresponding EDS mapping on the polished surface of (Cu0.93Ag0.07)2Se pellet, (e) high-magnification BSE images on the polished surface of the (Cu0.93Ag0.07)2Se pellet, the inset is enlarged image of the orange square circled area.
$\sigma$, $S^2\sigma$ at 773 K (Fig. 1c) has reduced for ~38%, from −6.9 W m$^{-1}$ K$^{-1}$ of \((\text{Cu}_{0.99}\text{Ag}_{0.01})_2\text{Se}\) to −5 W m$^{-1}$ K$^{-1}$ of \((\text{Cu}_{0.93}\text{Ag}_{0.07})_2\text{Se}\). With increasing $x$ from 0.01 to 0.07 in \((\text{Cu}_{1-x}\text{Ag}_x)_2\text{Se}\), the sharply dropped $D$ (Fig. S1b) leads to the dramatically reduced $\kappa$ (Fig. 1d). This is due to the decreased $\kappa_l$ (Fig. 1e) from −0.42 W m$^{-1}$ K$^{-1}$ of \((\text{Cu}_{0.99}\text{Ag}_{0.01})_2\text{Se}\) to −0.23 W m$^{-1}$ K$^{-1}$ of \((\text{Cu}_{0.93}\text{Ag}_{0.07})_2\text{Se}\) at 773 K. The obtained peak $zT$ of \((\text{Cu}_{0.99}\text{Ag}_{0.01})_2\text{Se}\) pellet is −0.9 at 773 K. In addition, with increasing $x$, the peak $zT$ of \((\text{Cu}_{0.93}\text{Ag}_{0.07})_2\text{Se}\) reaches −1.1 at 773 K (Fig. 1f) due to the reduced $\kappa_l$.

To understand the variation of thermoelectric performance in our sintered \((\text{Cu}_{1-x}\text{Ag}_x)_2\text{Se}\) pellets as a function of $x$, we performed detailed structural and compositional characterizations. Fig. 2a is the XRD patterns taken from the sintered pellets with $x = 0.01, 0.03$ and 0.07, respectively. As can be seen, main phase of the pellets can be indexed as $\alpha$-Cu$_2$Se (Standard Identification Card, JCPDS: 47-1448). The $\alpha$-Cu$_2$Se has a crystallographic orientation along 410° plane indicated by stronger peak intensity. Similarly, relatively peak intensity of the 090° peak of $\alpha$-Cu$_2$Se is stronger comparing with standard card while the 541° peak slightly weaker. These suggests a preferred orientation along the 090° planes. Small amounts of Cu$_2$O (Standard Identification Card, JCPDS: 05–0667) and CuAgSe (Standard Identification Card, JCPDS: 25–1180) can be detected in \((\text{Cu}_{1-x}\text{Ag}_x)_2\text{Se}\) pellets with $x = 0.03$ and 0.07, suggesting that Ag might have surpassed the solubility limit to form secondary phase(s). The small amount of Cu$_2$O should have only

![Fig. 3. Temperature (T)-dependent carrier transport properties of sintered (Cu$_{1-x}$Ag$_x$)$_2$Se pellets (x = 0.01, 0.03 and 0.07): (a) carrier concentration ($n_H$), (b) carrier mobility ($\mu_H$), (c) reduced Fermi level ($\eta$), (d) effective mass ($m'$), (e) deformation potential ($E_{def}$) and (f) Lorenz factor ($L$).](image-url)
limited influence on thermoelectric performance of as-sintered (Cu1, xAg2)2Se pellets [27]. Detailed discussion about this can be found in Page 7 of the Supporting Information (Figs. S7 and S8). Fig. 2b shows the enlarged 071* and 090* diffraction peaks of α-Cu2Se. No obvious peak shift can be observed, indicating no obvious lattice change. Fig. 2c exhibits the enlarged 002* and 150* peaks of α-CuAgSe. It clearly reveals that no detectable CuAgSe when x = 0.01. With increasing x (from 0.01), the peak intensity of CuAgSe dramatically enhanced, indicating an increasing amount of CuAgSe. Ag solubility limit in our (Cu1, xAg2)2Se pellets was measured ~1 at. % as discussed in Fig. S2-S5. To understand the distribution of CuAgSe secondary phase, we performed low magnification BSE (backscattered electron) image together with EDS mappings for the (Cu0.93Ag0.07)2Se pellet and the results are shown in Fig. 2d. As can be seen, the bright areas reveal widely and homogeneously distributed secondary phase in the darker CuSe matrix. Ag, Se and Cu EDS mappings indicate that these bright areas are Ag-rich. Point analyses results (Fig. S4 and S5) and enlarged EDS mappings were shown in Fig. S12 of the Supporting information, which clearly reveals the Ag-rich secondary phase being CuAgSe, which is closely consistent with XRD results. To estimate the rough ratio of the bright areas in the BSE image of Fig. 2d, we used imagej software to calculate the ratio of bright and dark areas and the result suggests that the secondary phase in (Cu0.93Ag0.07)2Se pellet has a ratio of ~7%. This value is close to the calculated phase content of CuAgSe in the (Cu0.93Ag0.07)2Se pellet (~6.6%) from XRD Rietveld refinement, shown in Fig. S3. Fig. 2e shows the high-magnification BSE images on the polished surface of the (Cu0.93Ag0.07)2Se pellet, in which the particle size of the CuAgSe secondary phase (bright area) can be estimated as ~1 μm. The composition analysis can be seen in Fig. S4 and S5. The observed dark areas are pores, detailed discussions can be seen in Page 5 of the Supporting Information. It should be noted that although α-Cu2Se has a cubic crystal structure and shows isotropic thermoelectric performance [1,17,21,28,29], the peak intensity of CuAgSe dramatically enhanced, indicated by CuAgSe secondary phase also changed the temperature-dependent scattering factor (r = −1/2 for acoustic phonon scattering) [26], Hall coefficient, effective mass, reduced plunk constant, elastic constant for longitudinal vibrations and deformation potential coefficient, respectively. The vH was taken as 3350 m s−1 [20]. F(η) is the Fermi integral expressed as

$$\eta_0 = \frac{1}{eK_t} = \frac{(2m^*\kappa_A T)^{3/2}}{3\pi^2h^3} \left( \frac{r + \frac{3}{2}}{r + \frac{5}{2}} \right) F_{r+\frac{1}{2}}(\eta)$$  \hspace{1cm} (2)$$

$$\mu_0 = \left[ \frac{ehn^4}{\sqrt{2(k_B T)^2E_{\text{def}}^2(m^*)^3}} \right] \left( \frac{r + \frac{3}{2}}{r + \frac{5}{2}} \right) F_{r+\frac{1}{2}}(\eta)$$ \hspace{1cm} (3)$$

$$L = \frac{\left( \frac{k_B}{e} \right)^2}{\int_0^\infty \frac{x^3}{1 + e^{x-v_H}} dx}$$ \hspace{1cm} (4)$$

where $\eta$, $\kappa_A$, $e$, $r$, $\mu_0$, $m^*$, $c$, $C_i$ ($C_i = v_i^2\rho_i$, $v_i$ and $\rho_i$ are the longitudinal sound velocity and density) and $E_{\text{def}}$ are the reduced Fermi level, Boltzmann constant, electron charge, carrier scattering factor, calculated from the single parabolic band model application in Cu2Se lies in three points, including a single valence band behaviour (indicated by a nearly temperature-independent $\eta_0$ shown in Fig. 3a), especially when x is low), acoustic phonon scattering-dominated carrier scattering mechanism ($\mu_0 \sim T^{-2/3}$ shown in Fig. 3b) and the assumption of a parabolic band due to a relatively large band gap (~0.6 eV) of [β-Cu2Se [24–26,32]. Fig. 3a and b shows the measured temperature-dependent $\eta_0$ and $\mu_0$. As can be seen, with increasing x, additional CuAgSe secondary phase has enhanced $\eta_0$. The increasing amount of alloyed CuAgSe has shifted the Fermi level closer to the valence (demonstrated by the dropped calculated reduced Fermi level with increasing x shown in Fig. 3c) and possibly flattened the band (indicated by the enhanced $m^*$ shown in Fig. 3d) and subsequently enhanced $\mu_0$ [9,33]. The enhanced $m^*$ also dramatically reduce $\mu_0$ (Fig. 3b). Additionally, in the (Cu0.93Ag0.07)2Se pellet, additional carrier scattering introduced by CuAgSe secondary phase also changed the temperature-dependency of $m^*$ and subsequently makes the exponent of $\mu_0$ to temperature smaller than −3/2 [34,35]. It should be pointed that the additional CuAgSe secondary phase has simultaneously slightly reduced the $E_{\text{def}}$ as shown in Fig. 3e which would theoretically lead to the enhanced $\mu_0$ [36]. Meanwhile, the influence of the reduced $E_{\text{def}}$ has been offset by

Fig. 4. Thermoelectric performance of as-sintered porous (Cu1, xAg2)2Se pellets (x = 0.01, 0.03 and 0.07) with respect to the amount of CuAgSe under 573, 623, 673, 723 and 773 K, respectively: (a) total thermal conductivity ($\kappa$) and (b) lattice thermal conductivity ($\kappa_L$).
the enhanced $\sigma_l$. The calculated $\sigma_l$ was also shown in Fig. 3f, where no obvious change has been observed due to different amount of CuAgSe. Here, $\sigma_l$ values reduces with increasing the temperature, leading to low $\kappa_l$ and subsequently slightly higher $\kappa$ at high temperature range. Similar results have also been observed in other studies [28,29,37,38]. Perhaps further theoretical study is necessary to get a better understanding on the underlying phonon scattering mechanism.

To clearly exhibit the influence of the CuAgSe secondary phase on thermoelectric performance of the sintered ($Cu_{1-x}Ag_x$)$_2$Se pellets ($x = 0.01, 0.03$ and $0.07$), we further plot $\kappa$ and $\kappa_l$ with respect to the amounts of CuAgSe measured under 573, 623, 673, 723 and 773 K in Fig. 4a and b. As can be seen, $\kappa_l$ of the Cu2Se measured under varying temperature are plotted in the Fig. S6 and S7. As can be seen, all these thermoelectric properties are strongly related with the amounts of CuAgSe. Specially, $\kappa$ is nearly linear with the amount of CuAgSe, suggesting that the CuAgSe secondary phase should be the key factor for the changed thermoelectric performance. The reduction of $\kappa_l$ of the sintered pellets with increasing the amount of CuAgSe is most likely related with the intrinsically low $\kappa_l$ of $\alpha$-CuAgSe (~0.2 W m$^{-1}$ K$^{-1}$) above 500 K [39]. Dominated by reduced $\kappa_l$, $zT$ at 773 K has been enhanced from ~0.9 of ($Cu_{0.99}Ag_{0.01}$)$_2$Se to ~1.1 of ($Cu_{0.93}Ag_{0.07}$)$_2$Se.

3.2. Reduced lattice thermal conductivity via porous design

It should be noted that the density of our sintered ($Cu_{1-x}Ag_x$)$_2$Se pellets is lower than the theoretical density. To better understand this difference, we plot the comparison of $\kappa$ and $\kappa_l$ between our pristine Cu2Se pellet and the high-density bulk Cu2Se shown in Fig. 5a and b [1]. As can be seen, $\kappa_l$ of our pristine Cu2Se pellet (~0.6 W m$^{-1}$ K$^{-1}$) is ~30% lower than that of the high-density bulk (~1 W m$^{-1}$ K$^{-1}$) for all the measuring temperature range. $\kappa_l$ of ~0.25 W m$^{-1}$ K$^{-1}$ is also lower than that of the bulk for the entire temperature range. Such a low $\kappa_l$ of our pristine Cu2Se should be attributed to the low relative density due to ~10% porosity due to pores of various sizes characterized by SEM analysis [29,37].

In order to characterize the pore structure of our samples, we use pristine Cu2Se pellet as a reference for SEM characterization and the results are shown in Fig. 6a and b. The widely distributed dark areas can be observed and indexed as pores. These pores have also been observed on the cross-section surface of sintered ($Cu_{1-x}Ag_x$)$_2$Se pellets (Fig. S8). As can be seen, large amounts of pores vary from nanoscale to several micrometres, which well explained the low relative density of our samples and subsequently low $\kappa_l$.

To understand formation of the pores in our samples, the synthesized Cu2Se powders were characterized by XRD and further compared with the sintered Cu2Se pellet, as shown in Fig. 7a. As can be seen, apart from the main $\beta$-Cu2Se phase (Standard Identification Card, JCPDS: 06-0680), additional Cu3Se2 (Standard Identification Card, JCPDS: 47-1745), Cu and Cu2O can be detected in the synthesized Cu2Se powders, while Cu3Se2 and Cu have not been observed in the sintered pellets except for small amount of Cu2O (Fig. 7a and Fig. S9). These results indicate that the impurities found in the synthesized powders (including Cu3Se2, Cu and Cu2O) can react to form Cu2Se during SPS. The impurity phase contents before and after SPS have been calculated on the basis of Rietveld refined XRD patterns, and the relative densities of the sintered ($Cu_{1-x}Ag_x$)$_2$Se pellets with respect to the reacted phase contents are plotted in Fig. 7b. As can be seen, the relative density of as-sintered pellets is strongly reacted with the reacted phase contents which suggest that the formation of pores is strongly related with the reaction between Cu, Cu3Se2 and Cu2O during SPS. The reason this reaction could happen during SPS should be attributed to the low melting point of Cu3Se2 (408 K). The melting of Cu3Se2 together with high pressure during SPS has promoted the contact and reaction between Cu3Se2, Cu and Cu2O, where Cu2O may have partly electrolyzed due to large current in SPS. After reaction, pores would remain partially at the original position of some impurity phases due to volume change.

4. Conclusion

In conclusion, we synthesized Ag-doped ($Cu_{1-x}Ag_x$)$_2$Se powders by a facile solvothermal method. After Ag has reached its solubility limit of ~1 at. %, further increasing x leads to the formation of CuAgSe secondary phase. Consequently, $\kappa_l$ is reduced, and in turn $zT$ is enhanced. An extreme low $\kappa_l$ of ~0.23 W m$^{-1}$ K$^{-1}$ has been observed in ($Cu_{0.93}Ag_{0.07}$)$_2$Se pellet. Such a low $\kappa_l$ leads to a peak $zT$ of ~1.1 at 773 K. This low $\kappa_l$...
is partially contributed from abundant pores formed by reaction of impurity phases, including Cu2O and Cu3Se2 during SPS. With the widely distributed pores, \( k_i \) of our sintered pristine Cu2Se (~0.25 W m\(^{-1}\) K\(^{-1}\)) is far lower than high-density bulk. We have clearly exhibited the effectiveness of CuAgSe secondary phase and pores on reducing \( k_i \) and enhancing \( zT \) of Cu2Se.

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Appendix A. Supplementary data

The ‘Supporting Information’ include supplementary discussion about the measured specific heat, thermal diffusivity, the discussion about Ag solubility, the Rietveld refinement details, further information of CuAgSe secondary phase on thermoelectric performance of \((\text{Cu}_1 - x \text{Ag}_x)_{2} \text{Se}\) pores on cross-section of surfaces and distribution of Cu2O in as-sintered \((\text{Cu}_1 - x \text{Ag}_x)_2 \text{Se}\) pellets, thermoelectric performance of undoped Cu2Se and enlarged EDS mapping on the polished surface of \((\text{Cu}_{0.93} \text{Ag}_{0.07})_2 \text{Se}\) pellet.

References


Fig. 7. (a) X-ray diffraction patterns of synthesized Cu2Se powder comparing with sintered Cu2Se pellet, (b) relative density of sintered pellets with respect to reacted phase contents (Cu in powders, reacted Cu2O and Cu3Se2) during spark plasma sintering.

