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Enhanced low temperature thermoelectric performance of Ag-doped BiCuSeO

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We investigated the physical properties of the silver doped layered oxyselenides BiCu_{1-x}Ag_xSeO ($x=0-0.4$), which crystallize in an unusual intergrowth structure with [Cu₂Se₂]²⁻ and [Bi₂O₂]²⁺ layers. The total thermal conductivity is decreased because the heavier Ag doping in BiCuSeO lattice decreased the lattice thermal conductivity. The undoped BiCuSeO exhibits a semiconducting behavior, and the Ag-doped BiCuSeO performs much improved electrical conductivity. Although Ag-doping causes a decreasing Seebeck coefficient, the significant increase of the electrical conductivity compensates the moderate decrease of the Seebeck coefficient, which leads to the strongly improved power factor values. Finally, the figure of merit is improved and reaches a maximum ~ 0.07 at 300 K for the sample BiCu_{0.7}Ag_{0.3}SeO. © 2014 AIP Publishing LLC.

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Solid-state cooling and power generation based on thermoelectric (TE) effects have potential applications in waste-heat recovery, air conditioning, and refrigeration. The efficiency of TE devices is determined by the materials' dimensionless figure of merit, defined as $ZT = (S^2/\rho\kappa)T$, where S , ρ , κ , and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively.¹⁻³ Among the TE materials, metal oxides have received increasing attention because of their low cost, high thermal and chemical stability, and environmental compatibility.^{4,5} However, the thermal conductivity of metal oxides is relatively high due to their simple crystal structure, large bonding energy and light constituting elements which yield weak phonon scattering, impeding obtaining the large ZT value.

Recently, a p -type layered oxychalcogenide BiCuSeO composed of conductive [Cu₂Se₂]²⁻ layers alternately stacked with [Bi₂O₂]²⁺ layers,⁶ was found to exhibit a very promising figure of merit ($ZT > 0.8$ at 923 K),^{7,8} which is much larger than other polycrystalline oxide systems such as p -type Ca₃Co₄O₉ ($ZT \sim 0.2$ at 973 K)⁹ or n -type SrTiO₃ ($ZT \sim 0.35$ at 1273 K),¹⁰ ZnO ($ZT \sim 0.4$ at 1273 K),¹¹ or In₂O₃ ($ZT \sim 0.45$ at 1273 K).^{12,13} A large number of jobs concerning the thermoelectric property were published.¹⁴⁻²⁶ Its promising thermoelectric performance mainly originates from its low thermal conductivity coupled to a moderate power factor ($PF = S^2/\rho$). A limitation of undoped BiCuSeO for thermoelectric applications is its rather high electrical resistivity, which could be improved by increasing the carrier concentration.¹⁴⁻¹⁹ Theory calculation has indicated that the conduction band minimum (CBM) of BiCuSeO is primarily contributed from Bi $6p$ orbitals,^{27,28} while the valance band maximum (VBM) of BiCuSeO is mainly resulted from the

hybridization between Cu- $3d$ and Se- $4p$. Thus, enhancing the hybridization of the cation and anion in the conductive CuSe layer may be another way to improve the conductivity in BiCuSeO. For example, BiCuTeO, which is obtained by the replacement of Se by Te in BiCuSeO, exhibits improved conductivity than BiCuSeO, because the hybridization between Cu- $3d$ orbital and Te- $5p$ orbital is larger and the carriers transfer more easily in CuTe layer.^{29,30} On the other hand, lowering the thermal conductivity without significantly reducing the power factor would result in the increase of ZT value. Since the transport properties that determine the material efficiency are strongly correlated, depending on the carrier concentration, band structure and lattice thermal conductivity, etc., the optimization of carrier concentration or band structure by doping to reduce the thermal conductivity and resistivity will be an effective way to improve the ZT value of BiCuSeO.

In this work, we studied the Ag-doping effect on the physical properties of BiCuSeO, the Ag-doping suppresses thermal conductivity and decreased resistivity, leading to an remarkable improvement of ZT value.

Polycrystalline BiCu_{1-x}Ag_xSeO ($0 \leq x \leq 0.4$) were prepared by solid-state reaction between Bi₂O₃, Bi, Cu, Ag, and Se. The raw materials were mixed and ground thoroughly in an agate pestle and mortar, and then the mixtures were pressed into pellets under 12 MPa. The pellets were sealed under vacuum ($< 10^{-4}$ Pa) in the silica tubes, which had been baked in dry box for 1-2 h at 150 °C. The ampoules were annealed at 400 °C for 10 h to make sure the reaction of selenium with the elemental metals completely. Then, they were heated to 600 °C with 1 °C/min and maintained at this temperature for 20 h. Finally, the furnace was shut down and cooled to room temperature naturally. The obtained samples were reground, pelletized, and heated for another 20 h at 700 °C followed by furnace cooling. Room temperature X-ray diffraction (XRD) characterization was performed

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using a Panalytical X'pert diffractometer by using a $\text{Cu-K}\alpha$ radiation. The electrical and thermal transport properties were measured in a commercial Physical Property Measurement System ($1.8\text{ K} \leq T \leq 400\text{ K}$, $0\text{ T} \leq H \leq 9\text{ T}$). The conventional four-probe methods were used for the transport property measurements. Due to the strong anisotropic properties,²⁴ all the samples are measured along the direction perpendicular to the pressing direction, and the sample size is about $8 \times 2.5 \times 1.2\text{ mm}^3$ (Length $\times$ Width $\times$ Height).

As shown in Fig. 1, the structure of BiCuSeO is built up by stacking $[\text{Cu}_2\text{Se}_2]^{2-}$ and $[\text{Bi}_2\text{O}_2]^{2+}$ layers alternatively along the c axis. Using the tetragonal structure with the space group P4/nmm , the XRD patterns for the whole series of $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ can be fitted very well (Figs. 2(a) and 2(b)). A small amount of CuBi_2O_4 phase was detected for the samples, which may be caused by the easy volatilization of Se. The fitted structural parameters are shown in Fig. 2(c). It can be seen that lattice constants a and c increase monotonically with increasing Ag content from 0 to 0.4, indicating that the Ag has been introduced into BiCuSeO . The strong increase of both a and c is consistent with the much larger ionic radius of Ag^+ ($1.26\text{ \AA}$) than that of Cu^+ ($0.96\text{ \AA}$). However, it is noteworthy that the relative increase of c is much larger than that of a . The anisotropic evolution of the unit cell parameters with Ag substitution can be related to the layered structure of these materials with different bonding strengths along two directions.

The temperature dependence of electrical resistivity $\rho(T)$ of $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ in the range of 2–300 K is shown in Fig. 3(a). It clearly shows that the undoped BiCuSeO exhibits a semiconducting behavior over the entire temperature range, whereas the Ag doping changes the electrical transport to metallic behavior gradually. The evolution of the electrical transport could be owing to two origins. First, the evolution of resistivity behavior could be originated from the evolution of the band structure. Fig. 3(b) shows the absorption spectra of $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$. The optical energy band gap, E_{gap} , was determined from the sharp decrease in the transmission region according to Tauc and Menth's law.³¹ It can be seen that the band gap shifts to lower energy with increasing Ag content, which is similar to the evolution of $\text{BiCuSe}_{1-x}\text{Te}_x\text{O}$.^{20,29} In undoped BiCuSeO , the CBM is primarily contributed from Bi $6p$ orbitals,^{27,28} while the VBM of BiCuSeO are mainly resulted from the hybridization

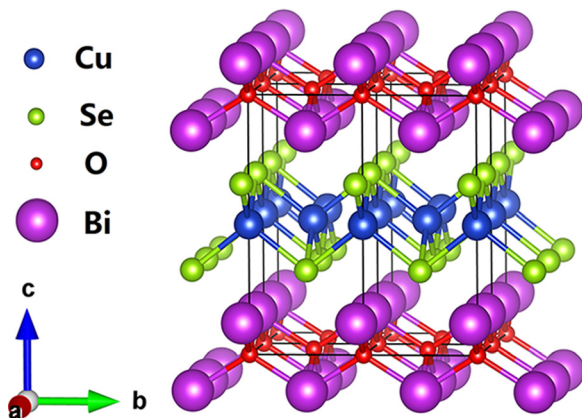


FIG. 1. The crystal structure of BiCuSeO .

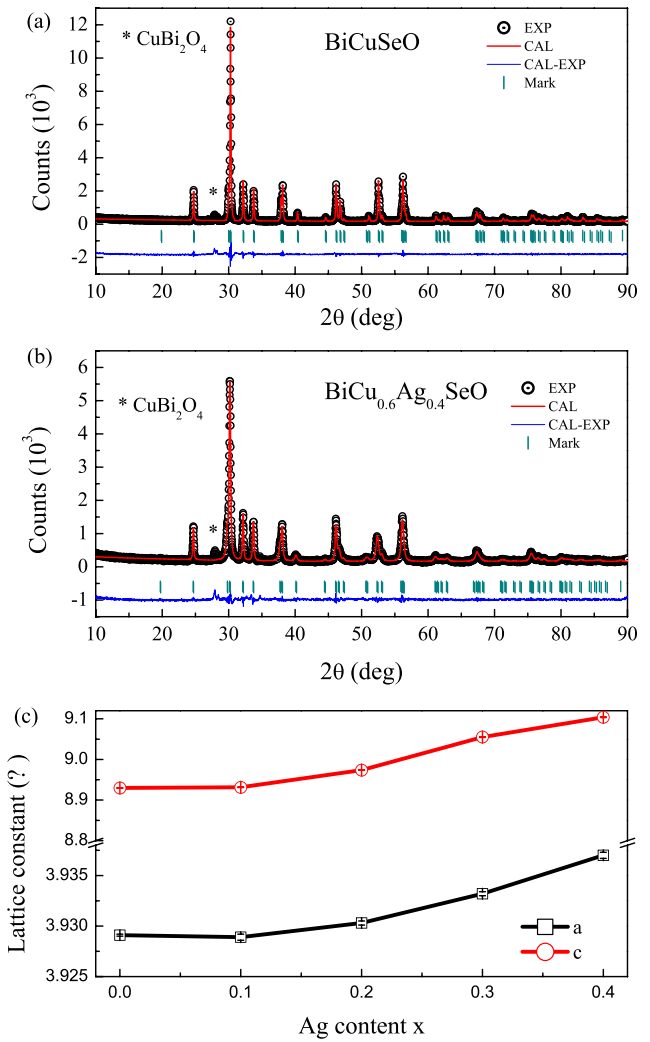


FIG. 2. (a) and (b) Rietveld refinement against powder XRD diffraction data for BiCuSeO and $\text{BiCu}_{0.6}\text{Ag}_{0.4}\text{SeO}$. (c) The fitted lattice parameters as a function of Ag content x .

between Cu-3d and Se-4p . The hybridization of Ag-4d and Se-4p should be larger than that of Cu-3d and Se-4p . Then the VBM of Ag-doped BiCuSeO would be shallower than that of undoped BiCuSeO , in which case the acceptor level would shift into the valence band (VB), generating a large number of holes and causing the metallic-like behavior in Ag-doped BiCuSeO . The idea is put forward by Hosono *et al.* to explain the metallic behavior in BiCuTeO .³⁰ On the other hand, in contrast to the semiconducting behavior of BiCuSeO in current work, metallic behavior is observed in the unintentionally doped BiCuSeO , probably due to a faint amount of Cu vacancy.⁸ As the large difference between the size of Cu ion and Ag ion, it is possible to introduce Cu/Ag-vacancy at Cu site in $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ as Ag is doped in the lattice. Thus, this could lead to the crossover of resistivity from semiconducting behavior to metallic one. All in all, the Ag-doping in BiCuSeO improves the electrical conductivity.

The Seebeck coefficients (S) of all the samples in the whole temperature range are positive, indicating p -type carriers are dominant (Fig. 4(a)). The Seebeck coefficient for undoped BiCuSeO is $357\text{ }\mu\text{V/K}$ at 300 K, which is consistent with the previous results.⁸ Ag-doping has a significant effect on the Seebeck coefficient, which decreased from $357\text{ }\mu\text{V/K}$

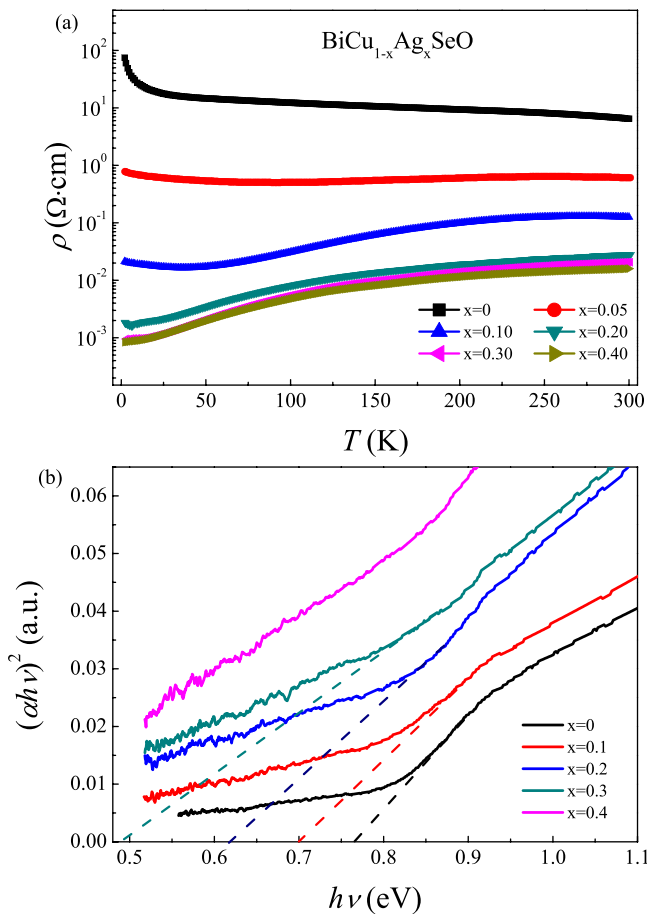


FIG. 3. (a) Electrical resistivity of $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ ($x=0-0.4$) is plotted as a function of temperature from 300 to 2 K. (b) The electronic absorption spectra of $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$. It is the plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$ and the band-gap energy is deduced from the extrapolation of the straight line up to $(\alpha h\nu)^2=0$.

for $x=0$ to $143 \mu\text{V/K}$ for $x=0.4$ at 300 K. There is an anomaly for $x=0.1$ that the Seebeck coefficient increases with decreasing temperature and reaches a maximum value $236 \mu\text{V/K}$ at about 100 K, the origin of which is unknown at present. With increasing Ag content, the significant decrease of the electrical resistivity compensates the moderate decrease of the Seebeck coefficient, which leads to strongly improved PF values (Fig. 4(b)). It is noteworthy that the PF does not increase monotonously with increasing Ag content, but reaches a maximum between $x=0.2$ and $x=0.3$. For the samples of $x \geq 0.2$ whose ground state are metallic-like, there is little improvement to the electric conductivity but the thermopower decreases continuously when the content of Ag further increases. Therefore, hole doping is a good approach to improve the thermoelectric properties and the optimization of the power factor can be reached at $x=0.2-0.3$.

Fig. 5 shows the temperature dependence of the thermal conductivity of $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ compounds. The total thermal conductivity values decrease remarkably with increasing Ag content. Generally, the total thermal conductivity can be expressed as a sum of lattice and electronic terms, i.e., $\kappa(T) = \kappa_L(T) + \kappa_e(T)$. We used the Wiedemann-Franz law to calculate the electronic term ($\kappa_e(T) = L\sigma T$, where $L = 2.44 \times 10^{-8} \text{ W } \Omega/\text{K}^2$ is the Lorenz number, σ is the electrical conductivity, and T is the absolute temperature). The

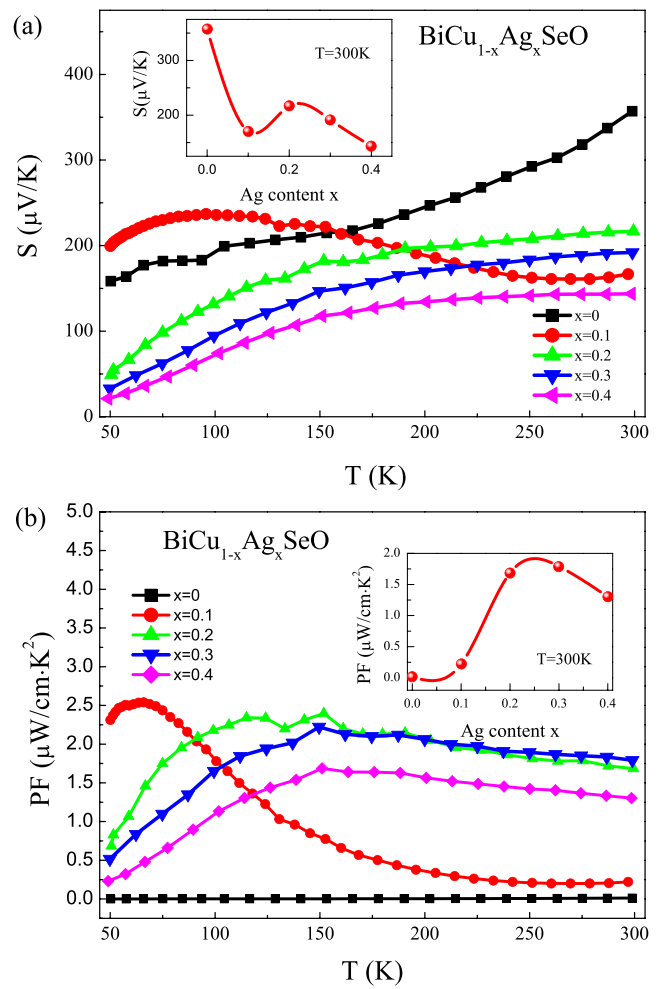


FIG. 4. Temperature dependence of the Seebeck coefficient (a) and power factor (b) of the series $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ ($x=0-0.4$). The inset shows the values at room temperature.

lattice contribution to the thermal conductivity is obtained by subtracting the electronic contribution from the total thermal conductivity. The κ_e is enhanced due to the increase of electrical conductivity but the enhancement is marginal when compared to the decrease of total thermal conductivity. It suggests that the κ_L decreases greatly with Ag doping, because the Ag in the Cu lattice of BiCuSeO plays a role as the strong phonon point defect scattering center due to a large mismatch between the size and mass of Ag and Cu atoms (160 pm and 108 g/mol for Ag versus 135 pm and 64 g/mol for Cu).

Temperature dependence of ZT values with Ag doping calculated based on the above transport data is presented in Fig. 6. The ZT values increase over the whole measured temperature except for the sample $\text{BiCu}_{0.9}\text{Ag}_{0.1}\text{SeO}$. The ZT value of our undoped BiCuSeO at room temperature is less than 0.001, which is due to the very low electrical conductivity. As Ag is doped, the ZT value is largely increased and reaches a maximum of 0.07 at 300 K for the sample $\text{BiCu}_{0.7}\text{Ag}_{0.3}\text{SeO}$. According to the expression of ZT , the enhanced value mainly benefits from the increased electrical conductivity and the reduced lattice thermal conductivity. Moreover, the optimization of the carrier concentration by hole doping to further increase the electrical conductivity of $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ ($x=0.2-0.3$) may be a good way to further improve the thermoelectric properties in this system.

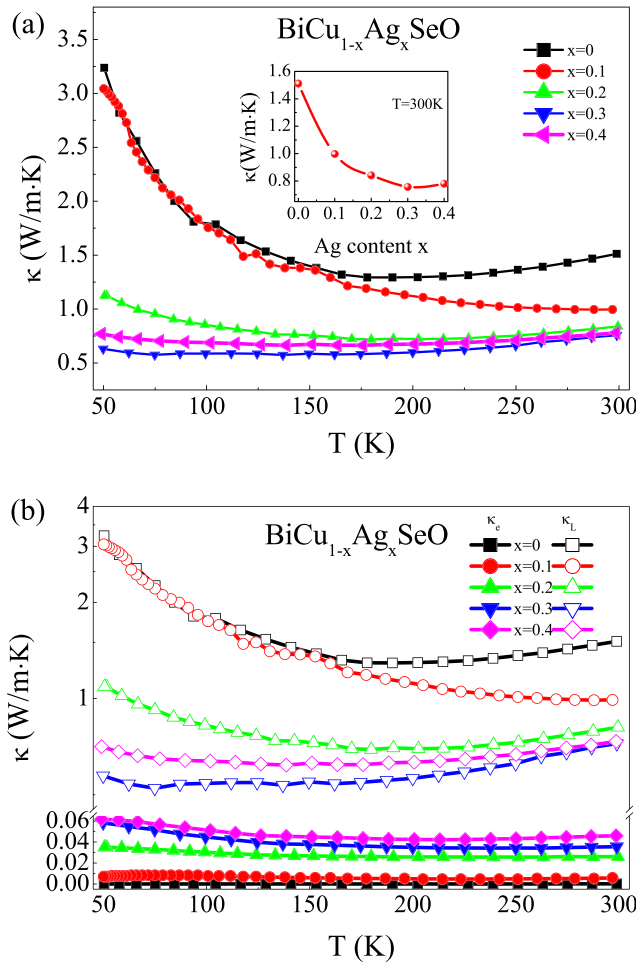


FIG. 5. (a) Temperature dependence of thermal transport properties for samples $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ ($x=0-0.4$). (a) Total thermal conductivity, the inset shows the values at room temperature; (b) lattice thermal conductivity (κ_L) and electronic thermal conductivity (κ_e).

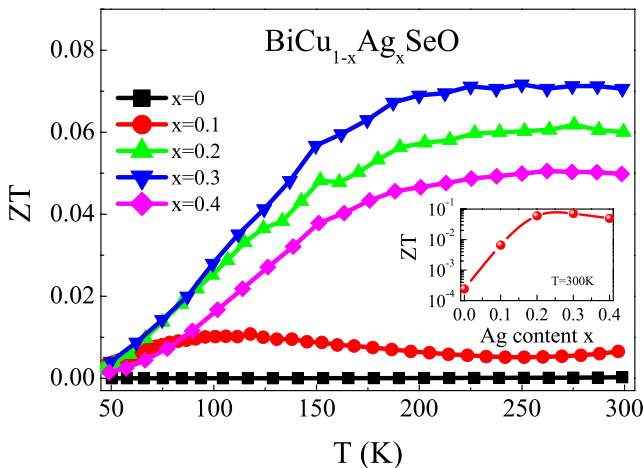


FIG. 6. Temperature dependence of the ZT value for the series $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ ($x=0-0.4$). The inset shows the ZT values at room temperature as a function of Ag content x .

In summary, the $\text{BiCu}_{1-x}\text{Ag}_x\text{SeO}$ ($0 \leq x \leq 0.4$) polycrystalline samples were synthesized by a solid state reaction. The electrical conductivity is largely improved by Ag doping. The Seebeck efficient decreases via Ag doping, but the significant decrease of the resistivity compensates the

moderate decrease of the Seebeck coefficient, which leads to the strongly improved PF values. Moreover, the heavier Ag doping decreases the lattice thermal conductivity and thus decreases the total thermal conductivity. As a result, a high ZT value up to ~ 0.07 at room temperature is achieved for the sample $\text{BiCu}_{0.7}\text{Ag}_{0.3}\text{SeO}$, which may be a candidate for TE materials at high temperature.

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