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$BaCu_2Se_2$ based compounds as promising thermoelectric materials

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ABSTRACT: In the past few years, many studies have been devoted to the thermoelectric properties of copper selenides and sulfides, and several families of materials have been developed with promising performances. In this paper, we report on the synthesis and thermoelectric properties of Na-doped $BaCu_2Se_2$ from 20K to 773 K. By Na doping at Ba site, the electric conductivity can be increased by 2 orders of magnitude, and the power factor can reach 8.2 $\mu Wcm^{-1}K^{-2}$ at 773K. Combined with a low thermal conductivity of 0.65 $Wm^{-1}K^{-1}$, ZT of 1.0 has been obtained for $Ba_{0.925}Na_{0.075}Cu_2Se_2$ at 773 K, which is the highest value reported in this family by now. However, the $BaCu_2Se_2$ volatilizes from 473K, so protecting coating is necessary for its application. Besides, we studied thermal expansion coefficient of $BaCu_2Se_2$ in this paper.

Introduction

Thermoelectric materials are currently receiving a significant scientific attention since they are capable of converting waste heat into electrical power. The power generation efficiency of a thermoelectric device is determined by the dimensionless figure of merit ZT, $ZT = (S^2\sigma/\kappa)T$, where S, σ, κ and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the absolute temperature, respectively. Several approaches to enhance ZT have emerged in the last decades,

most of these approaches aim to gain a high power factor ($S^2\sigma$) while obtaining a low lattice thermal conductivity (κ). Alternatively, one can also seek high thermoelectric performance in pristine materials with intrinsically low thermal conductivity. Copper-containing chalcogenides have been in the limelight of solid state research due to their large variety of crystal structures[1-4] and potential for widespread applications, including magnetic semiconductor,[5] high-Tc superconductors,[6] or transparent conductor[7]. Recently, copper chalcogenides based materials have attracted extensive interest in the thermoelectric community due to low thermal conductivities, which lead to the promising excellent thermoelectric properties: BiCuSeO[8] (κ~0.6 $Wm^{-1}K^{-1}$, ZT~1.4 for textured Ba-doped sample at 923K), $Cu_2CdSnSe_4$ (κ~0.8 $Wm^{-1}K^{-1}$, ZT~0.65 at 773K)[9], $Cu_2ZnGeSe_4$[10] (κ~0.8 $Wm^{-1}K^{-1}$, ZT~0.45 at 670K), $Cu_2ZnSnSe$[11] (κ~0.8 $Wm^{-1}K^{-1}$, ZT~0.91 at 860 K), $Cu_3Sb_{1-x}Sn_xSe_4$[12] (κ~1.0 $Wm^{-1}K^{-1}$, ZT~1.05), Cu_2SnSe_3[13] (κ~0.74 $Wm^{-1}K^{-1}$, ZT~0.33 at 650K), CuAgSe[14a, b)] (κ~0.47 $Wm^{-1}K^{-1}$, ZT~0.95 at 623 K), CuAgS[14c)] (κ~0.52 $Wm^{-1}K^{-1}$ at 550 K), Cu_2Se[15a)] (κ~1 $Wm^{-1}K^{-1}$, ZT~1.5 at 1000K,), Cu_2S[15b)] (0.6 $Wm^{-1}K^{-1}$, ZT~1.7 at 1000K), $Cu_{12}Sb_4S_{13}$[16](κ~ 1.5 $Wm^{-1}K^{-1}$, ZT above 0.8 at 700K), $CuInTe_2$[17](κ~1 $Wm^{-1}K^{-1}$, ZT~1.18 at 850K), and $CuGaTe_2$[18] (κ~1.35×10^{-3} $Wm^{-1}K^{-1}$, ZT~1.4 at 950K).

Herein, we report our results on another copper chalcogenide, $BaCu_2Se_2$ system. The crystal structure and transport properties of $BaCu_2Ch_2$ (Ch=S, Se and Te) have been studied by few groups to date.[19-26] For Ch = S and Se, two structure-types can be stabilized: the orthorhombic $BaCu_2S_2$-type and tetragonal $ThCr_2Si_2$-type.[20-23] Only the $BaCu_2S_2$ structure has been reported for $BaCu_2Te_2$ [20-23]. The electrical conductivity of β-$BaCu_2S_2$ and α-$BaCu_2Se_2$ is moderate, 49 Scm^{-1} [20], 5.5 Scm^{-1} [21], respectively, and 125 Scm^{-1} for $BaCu_2Te_2$ [21]. The electric conductivity can be improved by 1 order of magnitude by K doping in β-$BaCu_2S_2$, but the influence of doping on the electrical properties of $BaCu_2Se_2$ has not been studied to date experimentally. All the three compounds exhibit high Seebeck coefficient S (216 μVK^{-1}, 390μVK^{-1} and 127μVK^{-1}) and low thermal conductivity κ, 0.86 $Wm^{-1}K^{-1}$ [20], 1.5 $Wm^{-1}K^{-1}$, and 2 $Wm^{-1}K^{-1}$ [21] for Ch= S, Se and Te respectively at room temperature (it is noteworthy that these later values were overestimated due to radiation losses during the measurement as they were measured in steady-state conditions, contrary to the former one that was measured using a Laser Flash method), which make them promising thermoelectric materials. Indeed, thermoelectric figure of merit ZT of 0.28 at 820K has been reported for K doped β-$BaCu_2S_2$. However, no investigation has

been reported up to now regarding the thermoelectric property of doped $BaCu_2Se_2$ above room temperature.

In this work, we choose Na as an acceptor dopant at Ba site, to optimize the carrier concentration and enhance the power factor of $BaCu_2Se_2$. Results show that the electric conductivity can be increased by 2 orders, and the power factor of 8.2 $\mu Wcm^{-1}K^{-2}$ at 773K was realized. Combined with a low thermal conductivity of 0.65 $Wm^{-1}K^{-1}$, ZT of 1.0 has been obtained for $Ba_{0.925}Na_{0.075}Cu_2Se_2$ at 773 K. The thermal stability and phase stability were studied up to 873 K.

Experimental details

The $Ba_{1-x}Na_xCu_2Se_2$ (x=0, 0.005, 0.01, 0.015, 0.02, 0.025, 0.05, 0.075 and 0.1) powders were prepared by a two-step solid-state route. In the first step, the BaSe precursor was synthesized by heating Ba bulk and Se powder in sealed evacuated silica tubes coated with carbon at 873K for 24h. The Na_2Se precursor was previously synthesized by heating Na bulk and Se powder in sealed silica tubes coated with carbon at 1173K for 5h. The obtained BaSe and Na_2Se powders were single phase as confirmed by X-ray diffraction measurements. Then the BaSe, Cu, Se and Na_2Se as starting materials were mixed in stoichiometric amount as given by the formula $Ba_{1-x}Na_xCu_2Se_2$.The thoroughly mixed powders were pressed into pellets and sealed in evacuated silica tubes coated with carbon, followed by heating at 958K for 48 h. The obtained bulks were ground into powders and then densified by spark plasma sintering (SPS-511S) at 723K during 10min using graphite molds and dies with a pressure of 100 MPa under argon to form disk-shaped samples of Ø 10 mm and 3 mm in thickness. The resulting density of the SPS processed samples was 94% of the theoretical density.

Room temperature X-ray diffraction (XRD) characterization was performed using a Panalytical X'Pert diffractometer by using a Cu−Kα1 radiation, with a Ge (111) incident monochromator and a X'celerator detector. High temperature XRD patterns were recorded using a Bruker D8 Advance diffractometer with an Anton Paar TTK chamber. Rietveld refinement was performed using FULLPROF software. Seebeck coefficient (S) and electrical resistivity (ρ) were measured on bars cut from the pellets, with typical size 10 × 2 × 2 mm^3. The S and ρ measurements from 20 to 300 K were performed simultaneously by the differential method with two T-type thermocouples by using the slope of ΔV–ΔT curve with gradients up to about 0.2

K/mm, by using a laboratory made system in a He-free cryostat. S and ρ from room temperature to 773 K were measured by Ulvac Riko ZEM-3 instrument (ZEM-3, ULVAC-RIKO, Japan) under a helium atmosphere. Hall effect measurements were performed in a Quantum Design Physical Properties Measurement System (PPMS) environment using a Keithley 2400 current source and a Keithley 2182A nanovoltmeter, under magnetic fields from -9T to 9T. The thermal diffusivity (D) was measured in a disk-shaped sample of Ø10mm and 1–2 mm in thickness by using a laser flash diffusivity method (NETZSCH, LFA457, Germany). The thermal conductivity (κ) was calculated by the equation $\kappa = DC_pd$. C_p from 300K to 400 K was measured using a Quantum Design physical properties measurement system (PPMS); C_p above 400K was estimated from liner extension of values as measured from 300K to 400 K. The density d was measured using the dimensions and weight.

Room temperature optical diffuse reflectance measurements were performed on finely ground powders to probe optical energy gap of the series. The spectra were collected in the Varian Cary 5000 double-beam, double-monochromator spectrophotometer (Ultraviolet-Visible absorption Spectra). Scanning electron microscopy (SEM) studies were performed using a Hitachi S-3400N VP-SEM equipped with an Oxford detector for energy dispersive X-ray spectroscopy (EDS). The samples used for SEM were polished using a suspension of 50 nm Al_2O_3 particles. Thermogravimetric analysis was performed using a Setaram Setsys Evo under an Ar atmosphere in the temperature range from room temperature to 873 K with a rate of 5 K min^{-1}.

Results and discussion

Fig. 1a) shows the observed XRD pattern and Rietveld refinement of undoped $BaCu_2Se_2$, which crystallizes in the $BaCu_2S_2$-type structure. The simulated pattern by the Rietveld method agrees very well with the measured XRD pattern as shown in the difference profile. The orthorhombic structure, drawn in Fig. 1b), consists of a three dimensional Cu–Se network with Ba atoms residing in channels along the b-axis. The $CuSe_4$ tetrahedra are connected by sharing both vertices and edges. The Cu atoms construct zigzag chains of $CuSe_4$ tetrahedra.

Fig. 2a) shows powder XRD patterns of all the Na doped $BaCu_2Se_2$ samples. All the peaks can be indexed by $BaCu_2Se_2$ characteristic peaks (PDF#79-1647), no second phase can be observed. The cell parameters for the undoped sample are a =

9.575 Å, b = 4.202 Å and c = 10.755 Å. Fig. 2b) shows the lattice parameter variations as a function of Na doping fractions. The radii of Na^+ (0.97Å) is much smaller than that of Ba^{2+} (1.34Å), however, only faint lattice parameter change can be observed with increasing Na doping fraction, which is probably related to the fact that the Ba atoms are located along the channels, the substitution of Ba with Na does not affect significantly the Cu-Se rigid network. This result is in good agreement with the previous report on K doped β-$BaCu_2S_2$.[20] The band gap of $BaCu_2Se_2$ is about 1.8 eV, as shown in Fig. 2c), consistent with the value determined by McGuire et al.[21] Indeed, the electronic band structure close to the top of the valence band originates mainly from Se-p and Cu-d states and is not influenced by the Na doping.

The scanning electron microscopy image and element mapping of $Ba_{0.9}Na_{0.1}Cu_2Se_2$ are shown in Fig. 3. The uniform distributions of Ba, Cu, Se and Na for the $Ba_{0.9}Na_{0.1}Cu_2Se_2$ samples suggest that the synthesized material is homogenous.

Assuming a simple electrons counting, the substitution of one Ba^{2+} atom by one Na^+ atom in $BaCu_2Se_2$ should lead to one hole transfer, as:

$$[Ba_{1-x}Na_x]^{(2-x)+}[Cu_2Se_2]^{(2+x)-} = [Ba_{1-x}Na_x]^{(2-x)+}([Cu_2Se_2]^{2-} + x.h^+] \quad (1)$$

The former value is much higher than the one that could be expected from a large band gap semiconductor. This difference most probably originates from the presence of a faint concentration of copper vacancies, similarly to the behavior observed in the BiCuSeO family[8].

As shown in Fig. 4a), the carriers concentration indeed increases from 1.7×10^{18} cm^{-3} for the undoped sample to 2.6×10^{20} cm^{-3} for the $Ba_{0.9}Na_{0.1}Cu_2Se_2$. Indeed, a copper vacancies concentration as low as 7.4×10^{-4} per unit cell would be sufficient to induce such a carriers concentration. Taken together, the elements distributions and the increase of carriers concentration with doping level indicate the Na was successfully introduced into the $BaCu_2Se_2$ lattice. The measured carriers concentration is lower than the nominal one (e.g. measured 2.6×10^{20} cm^{-3} vs. nominal 9.2×10^{20} cm^{-3} for $Ba_{0.925}Na_{0.075}Cu_2Se_2$), estimated by taking into account the unit cell volume and the nominal Na concentration and assuming one free hole per Na atom. This difference could possibly be explained by Na loss during the synthesis. However, it could also be an indication of a poor doping efficiency of Na due to its much smaller ionic size as compared to Ba, which would lead to poor charge transfer to the Cu-Se network. Thus, it would be interesting to compare the doping efficiency of Na^+ and K^+ in $BaCu_2Se_2$, the ionic radius of K^+ being very close to that of Ba^{2+}.

As the substitution of Ba^{2+} by Na^{+} hardly affects the Cu-Se conducting network, the holes' mobility is almost constant in the whole series, of the order of μ = 10-15 $cm^2V^{-1}s^{-1}$ at room temperature, consistent with the value reported by McGuire et al.[21] in the undoped compound. The Fig. 4b) shows the typical temperature behavior of the holes mobility (here for Na=0.02), with a decreasing trend characteristic of degenerate semiconductors.

Fig. 5 shows the temperature dependences of electrical conductivity, Seebeck coefficient, and power factor for $Ba_{1-x}Na_xCu_2Se_2$ samples from 20 K to 773 K. The electrical conductivity of the undoped $BaCu_2Se_2$ is 3.1 Scm^{-1} at 300 K, consistent with the value obtained by McGuire et al.[21] In the entire temperature measurement range, Fig. 5a) and b), the electrical conductivity increases with increasing Na content, reaches a maximum of 420 Scm^{-1} at room temperature for $Ba_{0.925}Na_{0.075}Cu_2Se_2$, and it seems to get saturated when x=0.1. For samples with $x \leq 0.015$, the increasing electrical conductivity with temperature indicates a semiconductor-like behavior, and change to a metallic-like behavior as $x > 0.015$. The sharp improvement of electrical conductivity with Na doping contents is consistent with the increased carrier concentration.

All samples show positive S values indicating p-type semiconducting behavior, Fig. 5c) and d), which is consistent with the positive Hall coefficient. At 20K, S of the undoped $BaCu_2Se_2$ is 20 μVK^{-1}, it increases with rising temperature and reaches a value of 349 μVK^{-1} at 300 K. The Seebeck coefficient decreases with increasing Na content to 73 μVK^{-1} for $Ba_{0.90}Na_{0.10}Cu_2Se_2$ sample at room temperature.

The temperature dependent power factor generally increases linearly with increasing temperature (Fig. 5e and f). The Na doped $BaCu_2Se_2$ samples show an enhanced power factor as compared to the undoped sample because of their strongly improved electrical conductivity. The highest power factor of 8.2 $\mu Wcm^{-1}K^{-2}$ is obtained at 773 K when x= 0.075. The uncertainty of the Seebeck coefficient and electrical conductivity measurements is 5% for instruments below and above 300K. Along with temperature discrepancy, the difference between end value of low temperature range and starting value of high temperature range is within error bar of the instruments.

Fig. 6a) shows the specific heat capacity of $BaCu_2Se_2$, the room temperature value measured by PPMS is consistent with the Dulong-Petit law. The specific heat capacity increases with temperature, and is slightly larger than Dulong-Petit. Thus, C_p

of all the samples above 400K was estimated from linear extension of the as measured values from 300 to 400K in order to get an upper limit. Therefore, the thermal conductivity presented here is probably slightly overestimated and constitutes an upper limit. Fig. 6 b) shows the thermal diffusivity as a function of temperature for $BaCu_2Se_2$ samples. At room temperature, the total thermal conductivity of the $BaCu_2Se_2$ sample is κ_{tot}=0.68 $Wm^{-1}K^{-1}$ as shown in Fig. 6 c), which is approximately 50% lower than the value of around 1.5 $Wm^{-1}K^{-1}$ obtained using a steady-state method which was probably overestimated due to the radiative heat losses, as underlined by McGuire et al.[21] The total thermal conductivity increases with increasing Na content is due to the enhanced electrical thermal conductivity. For all samples, the total thermal conductivity decreases with increasing temperature, as expected for crystalline compounds with umklapp phonons scattering.

The lattice thermal conductivity, κ_{lat}, was estimated by subtracting the electronic part, κ_{ele}, from the κ_{tot} according to the Wiedemann-Franz law. The Lorenz number L can be estimated by fitting of the respective Seebeck coefficient to estimate the reduced chemical potential (η). The lattice thermal conductivity is dominant for all samples, and roughly obeys a T^{-1} relation (inset in Fig. 6e), which can be attributed to umklapp-processes being predominant at elevated temperatures. As shown in Fig. 6e), the lattice thermal conductivity slightly decreases with increasing Na content because of point defects scattering caused by the size and the atom mass difference between Na and Ba. The lattice thermal conductivity of $BaCu_2Se_2$ is much lower than the observed 1.5 $Wm^{-1}K^{-1}$ at room temperature[27,28] in Phonon Glass Electron Crystal (PGEC) materials like skutterudites and clathrates and is of same order of BiCuSeO[8]. Beside the large average atomic mass of $BaCu_2Se_2$ (84.47g/mol atom) and its quite complex and large unit cell, which are generally associated with low thermal conductivity [29-32], the peculiar crystal structure could also play a role. The phonons propagation in this family of materials should be mostly driven by the Cu-Se framework. Ba atoms lie in the middle of 1D channels inside this framework and could lead to low energy modes which would reduce heat propagation. It is believed that the lattice dynamic studies would be of fundamental interest in order to understand the original reasons of low thermal conductivity.

The power factor values obtained in Na-doped $BaCu_2Se_2$ are lower than the ones observed in state-of-the-art thermoelectric materials: PbTe (PF~25 $\mu Wcm^{-1}K^{-2}$, ZT~1.6-2.0) [33-35], PbSe (PF~14 $\mu Wcm^{-1}K^{-2}$, ZT~1.2)[36], Bi_2Te_3 (PF~30$\mu Wcm^{-1}K^{-2}$,

ZT~1.1-1.75)[37, 38]. However, the low thermal conductivity contributes to a high ZT of 1.0 at 773K for $Ba_{0.925}Na_{0.075}Cu_2Se_2$, Fig. 6f), which is probably underestimated (due to Cp estimation). This value is promising in a new compound, and ZT could be further enhanced through carriers concentration optimization.

To highlight the potential application of $BaCu_2Se_2$, the properties of thermal expansion and thermal stability are also as same important as a figure of merit. Fig. 7a) shows the XRD patterns of $BaCu_2Se_2$ recorded from room temperature to 873K under argon atmosphere. No new structure can be observed up to 773K, and only a shift of the Bragg peaks can be noticed originating from lattice expansion. However, a few impurity peaks occur above 823K (easily observed around $2\theta=25°$), indicating a decomposition of the $BaCu_2Se_2$ phase. Fig. 7b) shows the temperature dependence of the lattice parameters, obtained from Rietveld refinement of the XRD patterns. a, b and c continuously increase with increasing temperature. As it could be expected from the crystal structure, the thermal expansion coefficient is slightly anisotropic as estimated from the temperature dependence of the lattice parameters, with a larger value in the b direction, and it decreases with increasing temperature, from 30×10^{-6} K^{-1} at room temperature to 20×10^{-6} K^{-1} at 873K for a and c, and from 37×10^{-6} K^{-1} at room temperature to 32×10^{-6} K^{-1} at 873K for b. These values limit the families of n-type materials that could be associated to $BaCu_2Se_2$ in a thermoelectric module, as their respective coefficient of thermal expansion should match well.

As mentioned in the experimental section, $Ba_{1-x}Na_xCu_2Se_2$ powders and pellets were synthesized under vacuum during the entire synthesis process. Therefore, there could be some issues about the stability of these compounds in ambient conditions, as Na could easily react with CO_2 or water. Fig. 8 a) shows the XRD patterns of $Ba_{0.9}Na_{0.1}Cu_2Se_2$ powder stored during one month in ambient condition, and of $Ba_{0.9}Na_{0.1}Cu_2Se_2$ put in water during one week at room temperature, respectively. Surprisingly, both XRD patterns are the same as the corresponding freshly prepared sample (Fig. 1), which indicates that the $Ba_{0.9}Na_{0.1}Cu_2Se_2$ are air and water stable. However, the compounds rapidly degrade when heated at moderate temperature. As it can be observed in Fig. 8b), $BaCu_2Se_2$ powder starts to volatilize at a temperature as low as 473K, and rapidly almost completely volatilizes above 623K (the horizontal straight line on the TGA curve at a weight loss of about -63% corresponds to the saturation of the analyzer).

The inset of Fig. 8b) shows the TGA at 523K of a SPSed $BaCu_2Se_2$ pellet, with a density of 94% of the theoretical density. Even with almost full density and at a moderate temperature, the sample volatilizes, with a weight loss as large as 0.1% after only 2h at 523K. This volatilization would preclude the use of these materials in real modules used for waste heat conversion at high temperature. Therefore, it would be of great interest to find some coatings to limit the volatilization of the material, similarly to the coatings that have been developed for n-type skutterudites to limit the volatilization of antimony and make them usable in thermoelectric modules [39].

Conclusion

Na-doped $BaCu_2Se_2$ samples were prepared by solid-state reaction followed by spark plasma sintering densification. All samples were p-type with large Seebeck coefficient and very low thermal conductivity. The electrical conductivity can be strongly improved from 3.1 Scm^{-1} for $BaCu_2Se_2$ to 440 Scm^{-1} for $Ba_{0.925}Na_{0.075}Cu_2Se_2$ at 300 K due to the increased carrier concentration, leading to an enhanced power factor of 2.7 $\mu Wcm^{-1}K^{-2}$ at 300K and 8.2$\mu Wcm^{-1}K^{-2}$ at 773K. A ZT of 1.0 has been achieved at 773 K for doped $BaCu_2Se_2$, which is the highest values reported in the $BaCu_2Ch_2$ (Ch=S, Se and Te) family. However, the low evaporation temperature, hardly larger than 473K, limits its potential in thermoelectric modules at high temperature and would require the development of protective coatings to limit the materials degradation.

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Figure Caption

Fig. 1 a) X-ray diffraction pattern and Rietveld refinement of $BaCu_2Se_2$ powder; b) Crystal structure of $BaCu_2Se_2$.

Fig. 2 a) XRD patterns; b) Lattice parameters of $Ba_{1-x}Na_xCu_2Se_2$ samples; c) Diffuse reflectance of $BaCu_2Se_2$.

Fig. 3 a) Scanning electron micrographs of $Ba_{0.9}Na_{0.1}Cu_2Se_2$; X-ray Element mapping images of b)Ba, c)Na, d)Cu, and e) Se in $Ba_{0.9}Na_{0.1}Cu_2Se_2$.

Fig. 4 a) Hall carriers concentration and mobility in $Ba_{1-x}Na_xCu_2Se_2$ series (the solid line corresponds to the nominal carriers concentration estimated assuming one free hole per sodium atom); b) Temperature dependence of the holes mobility of $Ba_{0.98}Na_{0.02}Cu_2Se_2$.

Fig. 5 Thermoelectric properties as a function of temperature for $Ba_{1-x}Na_xCu_2Se_2$ samples: a), b) Electrical conductivity; c), d) Seebeck coefficient and e), f) Power factor.

Fig. 6 Thermoelectric properties as a function of temperature for $Ba_{1-x}Na_xCu_2Se_2$ samples: a) Specific heat; b) Thermal diffusivity; c) Total thermal conductivity; d) Lattice thermal conductivity; e) Electric thermal conductivity; and f) Figure of merit ZT.

Fig. 7 a) XRD patterns of $BaCu_2Se_2$ as a function of temperature; b) Temperature dependence of the lattice parameters.

Fig. 8 XRD patterns of $Ba_{0.9}Na_{0.1}Cu_2Se_2$ a) after one month storage in ambient conditions and after one week in water; b) Thermogravimetric analysis of $BaCu_2Se_2$ powder and densified pellet (inset).

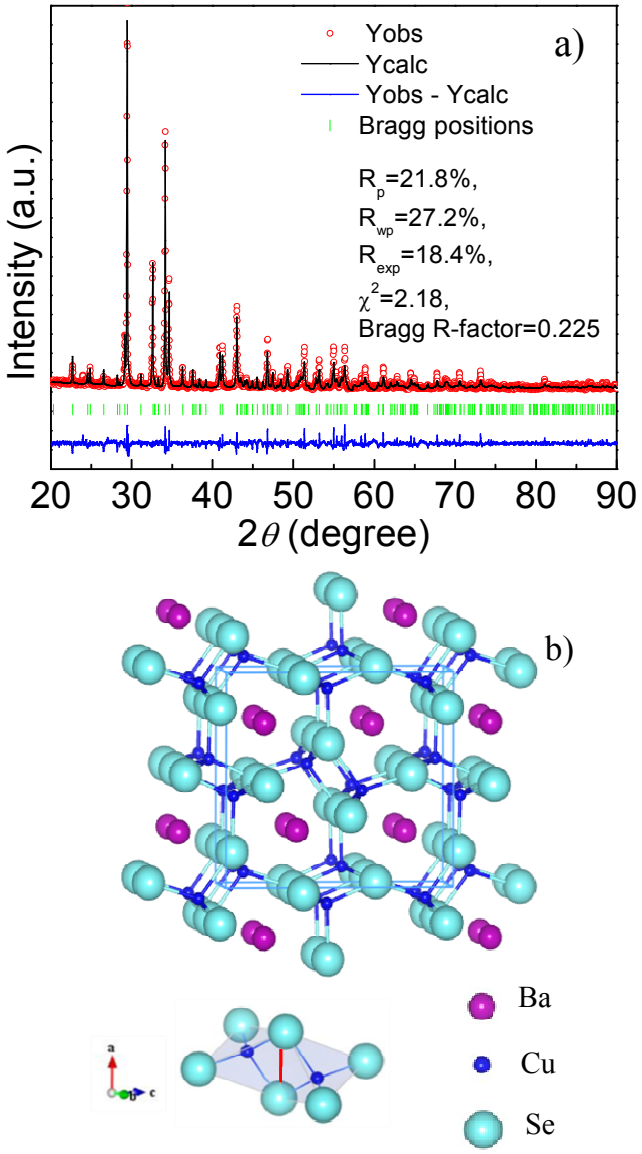

Fig. 1

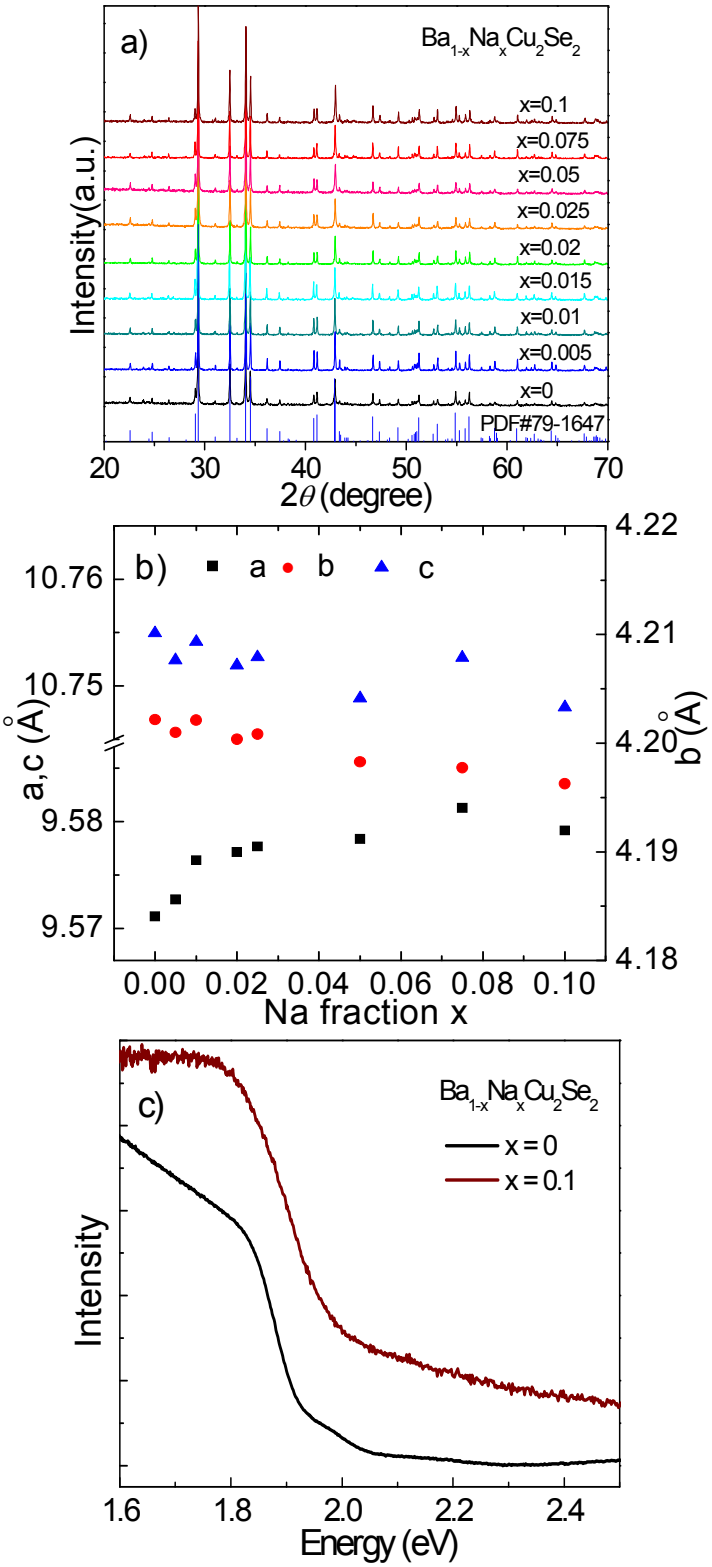

Fig. 2

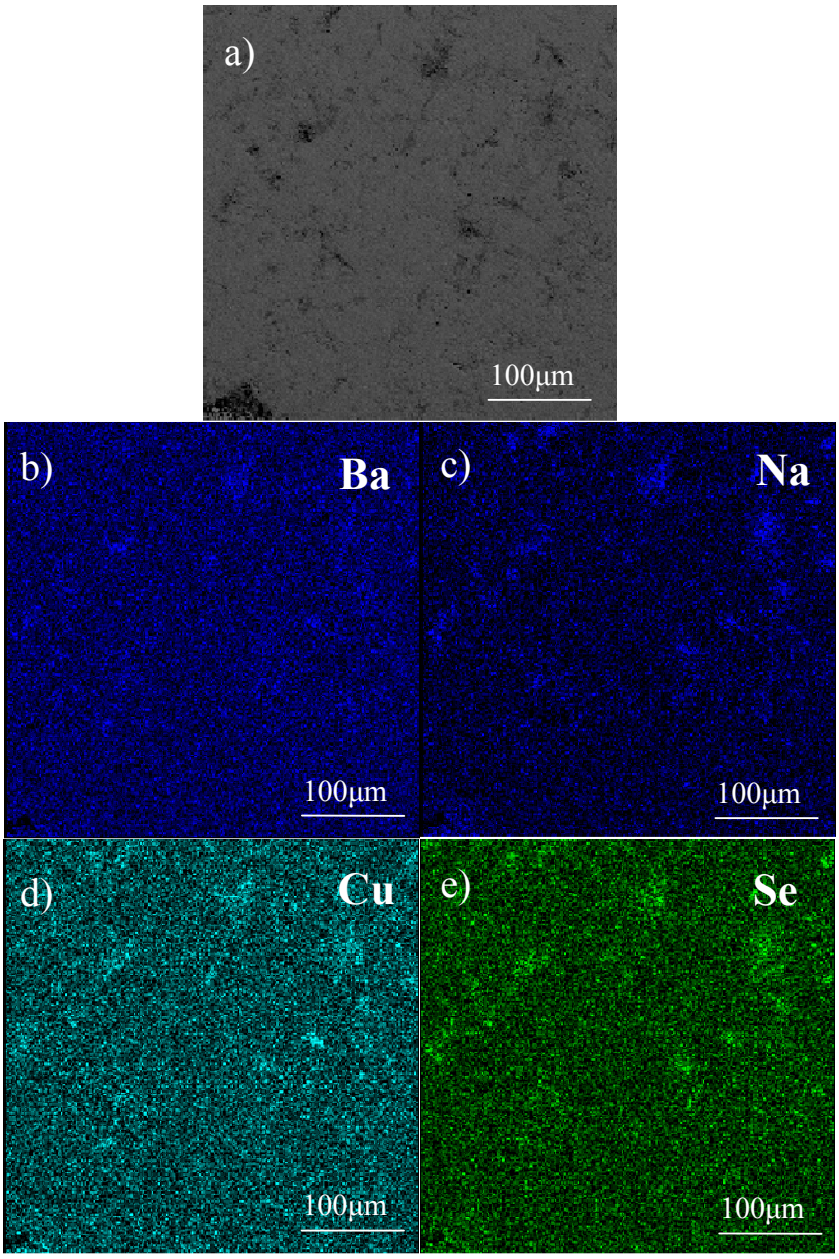

Fig. 3

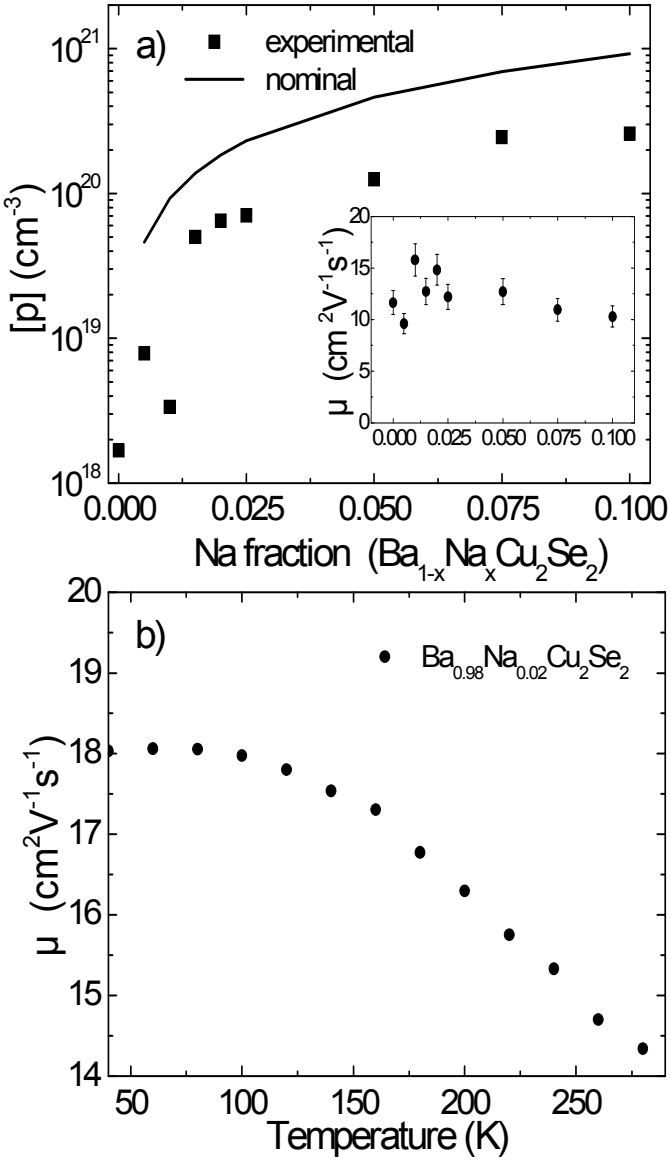

Fig. 4

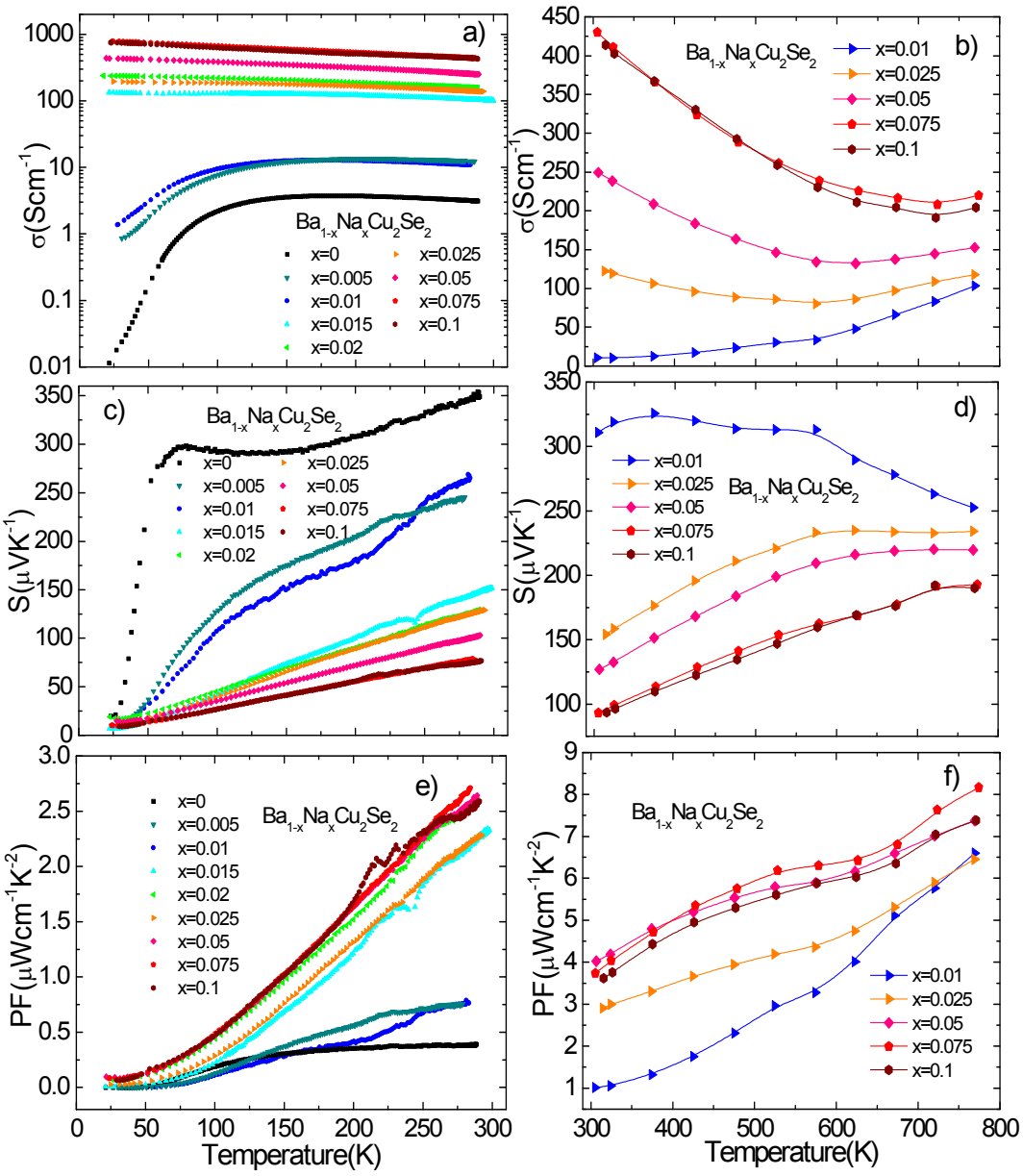

Fig. 5

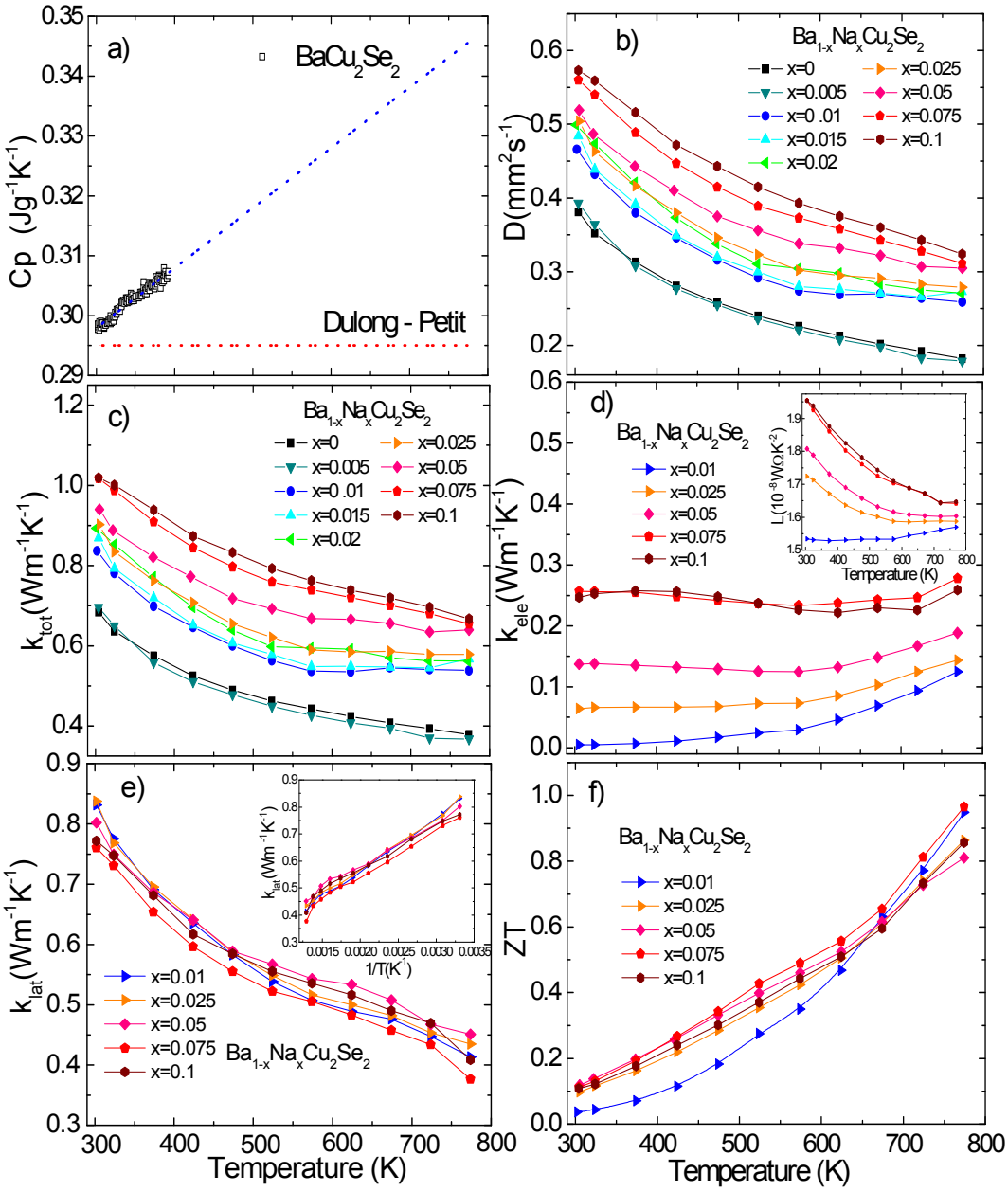

Fig. 6

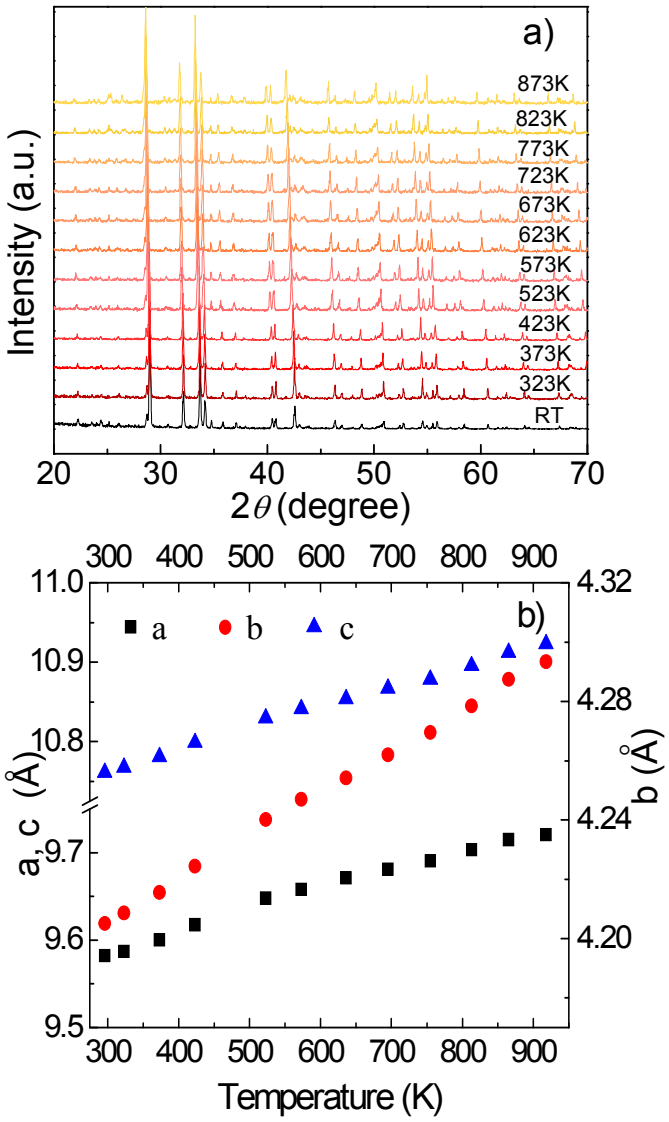

Fig. 7

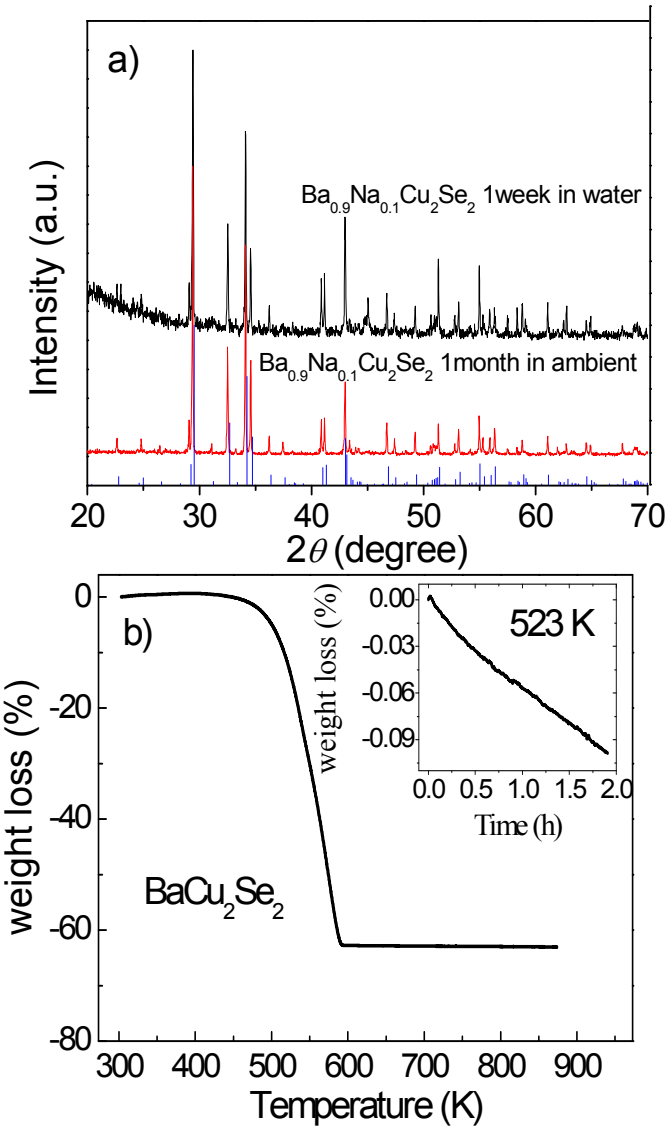

Fig. 8

Graphical Abstract

Thermoelectric properties of Na doped $BaCu_2Se_2$ was studied. The electric conductivity of $BaCu_2Se_2$ was increased by 2 orders of magnitude through Na doping at Ba sites, combined with a surprisingly low thermal conductivity, ZT of 1.0 has been obtained for $Ba_{0.925}Na_{0.075}Cu_2Se_2$ at 773K.