n-Type thermoelectric metal chalcogenide \((Ag,Pb,Bi)(S,Se,Te)\) designed by multi-site-type high-entropy alloying

Aichi Yamashita\(^a\), Yosuke Goto\(^a\), Akira Miura \(^b\), Chikako Moriyoshi\(^c\), Yoshihiro Kuroiwa\(^c\) and Yoshikazu Mizuguchi\(^a\)

\(^a\)Department of Physics, Tokyo Metropolitan University, Tokyo, Japan; \(^b\)Faculty of Engineering, Hokkaido University, Hokkaido, Japan; \(^c\)Graduate School of Advanced Science and Engineering, Hiroshima University, Hiroshima, Japan

ABSTRACT

A metal chalcogenide \((Ag,Pb,Bi)(S,Se,Te)\) with a NaCl-type structure was designed by multi-site-type high-entropy alloying (MST-HEA), and the thermoelectric properties were investigated. In this material, both cation and anion sites were alloyed and thus its total entropy of mixing \(\Delta S_{\text{mix}}\) (total) achieved 2.00 \(R\) (\(R\) = gas constant). It was found that present sample is an n-type semiconductor with ultra-low lattice thermal conductivity \((\kappa_L)\) of 0.62 \(\text{Wm}^{-1}\text{K}^{-1}\) at room temperature and 0.46 \(\text{Wm}^{-1}\text{K}^{-1}\) at \(T = 723\) K. Very low \(\kappa_L\) and good power factor resulted in figure of merit of 0.54 at \(T = 723\) K.

IMPACT STATEMENT

We report on the material design synthesis and thermoelectric properties on new high-entropy alloy-type compound with an NaCl-type structure \((Ag,Pb,Bi)(S,Se,Te)\)

Introduction

Thermoelectric generators have attracted much attention due to their direct conversion of heat into electricity vice versa. The conversion efficiency of a thermoelectric material depends primarily on the dimensionless figure of merit, \(ZT = (S^2T\rho^{-1}\kappa_{\text{total}}^{-1})\), where \(S\), \(T\), \(\rho\) and \(\kappa_{\text{total}}\) are the Seebeck coefficient, absolute temperature, electrical resistivity and thermal conductivity, respectively [1]. \(\kappa_{\text{total}}\) has two main components, namely \(\kappa_e\) and \(\kappa_L\), which are carrier and lattice thermal conductivity, respectively. To realize the high \(ZT\) value, it is obvious that low \(\rho\) and high \(S\) are essential, although they depend on the carrier concentration and contradict each other. Another main strategy is realization of low \(\kappa_L\) because \(\kappa_L\) is independent of the electronic properties.

Metal chalcogenides (MCh) such as lead chalcogenides (PbTe, PbSe, PbS) have extensively studied as a thermoelectric system available at medium temperature (500–900 K) range [2–4]. The attempts to enhance the thermoelectric properties of MCh have been made by nano-structuring [5] and phase solution of pseudo-binary PbTe-PbSe [6–8] and ternary PbTe–PbSe–PbS [9,10] alloys, which achieve low \(\kappa_L\) and lead to improvements in power factor by band convergence [1,6,7]. In addition to the above-mentioned strategy, the introduction of bonding heterogeneity and the enhancement of lattice anharmonicity have been reported in AgPbBiSe\(_3\) [11] with quite low \(\kappa_L\) of 0.50 \(\text{Wm}^{-1}\text{K}^{-1}\) at room temperature and 0.41 \(\text{Wm}^{-1}\text{K}^{-1}\) at 818 K. The fundamental origin of this ultra-low \(\kappa_L\) is originated from the synergistic presence of bonding heterogeneity and lattice anharmonicity arising from 6s\(^2\) lone pairs of Bi and Pb [11].

As a brand-new method of alloying, high-entropy alloys (HEAs) have attracted much attention in the fields of materials science and engineering because of their tunable properties as structural materials, such as excellent mechanical performance under extreme conditions [12,13]. HEAs are typically defined as alloys containing at least five elements with concentrations between 5 and 35 at\%, resulting in high configurational mixing entropy (\(\Delta S_{\text{mix}}\)), defined as \(\Delta S_{\text{mix}} = -R\sum_i c_i \ln c_i\), where \(c_i\) and \(R\) are the compositional ratio and the gas constant, respectively [13]. Most of HEA materials are structurally simple alloys with bcc, \(\alpha\)-Mn, CsCl, and hcp crystal structures have mainly been studied so far [12–14]. Thus far, we have extended the concept of HEA to compounds, for instance layered structure and non-layered compounds.

CONTACT
Yoshikazu Mizuguchi
mizugu@tmu.ac.jp
Department of Physics, Tokyo Metropolitan University, 1–1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

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of NaCl-type metal chalcogenide, as superconductors with high $\Delta S_{\text{mix}}$ [15–22]. Furthermore, as an efficient way to increase total entropy of mixing, we proposed multi-site alloying of compounds and its evaluation way by summing the entropy of mixing at each alloying site [20]. A higher $\Delta S_{\text{mix}}$, which exceeds the typical $\Delta S_{\text{mix}}$ for equimolar 6 elements for single site, is achieved by this method. It is well known that alloying is the effective way to reduce $\kappa_L$ due to the enhancement of scattering of phonons by lattice disorder [8,23]. Based on this fact, the high-entropy alloying by the multi-site alloying method also could be the effective way to reduce the $\kappa_L$, for instance, by introducing the severe lattice distortion [24].

As HEA thermoelectric materials, AlCoCrFeNi [25] was first reported by Shafeie et al. in 2015. However, the $ZT$ values are low due to the high $\sigma$, low $S$ and high $\kappa$. After the report, some papers incorporating the HEA concept into thermoelectric materials have been reported: such as half-Huesler; NdFeSb-based [26], Ti2NiCoSnSb [27] and MChH; AgSnSbSe3–xTex [28]. Among them, AgSnSbSe3–xTex exhibited high $ZT$ values of 1.14 at 723 K as $p$-type thermoelectric materials. Very recently, $n$-type $MCh$ of Pb0.99–ySby0.012Sn0.2Se1–2xTex0.2x was reported with significantly high $ZT$ values of 1.8 at 900 K [29]. On this basis, we aimed to synthesize new NaCl-type $MCh$ with higher $\Delta S_{\text{mix}}$ value.

In this letter, we synthesized a high-entropy alloy-type (Ag,Pb,Bi)(S,Se,Te) by inducing alloying an anion site of $n$-type AgPbBiSe3 with low $\kappa_L$. Hereafter, we denote the concept that alloying multiple crystallographic site as ‘multi-site-type high-entropy alloying (MST-HEA)’. We successfully synthesized MST-HEA (Ag,Pb,Bi)(S,Se,Te) with highest $\Delta S_{\text{mix}}$ (total) value of 2.00$\Omega$ as a thermoelectric material to the best of our knowledge. It was found that the present sample was an $n$-type semiconductor with ultra-low $\kappa_L$ of 0.62 Wm$^{-1}$K$^{-1}$ at room temperature, and it reached 0.46 Wm$^{-1}$K$^{-1}$ at 723 K. Compared to AgPbBiSe3, the present sample exhibited lower $\rho$ without large decrease of $S$, resulted in the enhancement of power factor and $ZT$. Our results indicate that the MST-HEA $MCh$ could be a promising $n$-type thermoelectric material.

**Experimental**

Polycrystalline sample of (Ag,Pb,Bi)(Te,Se,S) was synthesized by congruent melt of Ag powders (99.9%) and grains of Pb (99.9%), Bi (99.999%), Te (99.999%), Se (99.999%) and S (99.999%) with a nominal composition of Ag0.25Pb0.50Bi0.25S0.40Se0.50Te0.10 at 800°C for 20 h after keeping at 400°C for 5 h to suppress an evaporation of chalcogen in an evacuated quartz tube. To obtain high-density samples, hot pressing was performed at 400°C for 30 min under a uniaxial pressure of 70 MPa, and subsequently, the furnace was cool down.

The density of hot-pressed sample was estimated from its weight and size. The relative density of sample was 97.4%. The actual composition was analyzed by energy-dispersive X-ray spectroscopy (EDX) on a TM-3030 (Hitachi Hightech) equipped with an EDX-SwiftED analyzer (Oxford). The phase purity and the crystal structure of the Ag0.25Pb0.50Bi0.25S0.40Se0.50Te0.10 sample were examined by powder synchrotron XRD with an energy of 25 keV ($\lambda = 0.495395$ Å) at the beamline BL02B2 of SPring-8. The synchrotron XRD experiments were performed at room temperature with a sample rotator system, and the diffraction data were collected using a high-resolution one-dimensional semiconductor detector MYTHEN [Multiple mythen system] [30] with a step of $2\theta = 0.006^\circ$. The crystal structure parameters were determined by Rietveld analysis using the RIETAN FP [31]. The crystal structure was depicted using VESTA [32].

To investigate the thermoelectric properties of sample, the electrical resistivity ($\rho$) and the Seebeck coefficient ($S$) were measured using the four-probe method under a helium atmosphere with a ZEM-3 (Advance Riko) instrument. The $\kappa_{\text{total}}$ was calculated using the equation $\kappa_{\text{total}} = DpCd$ where $D$, $C_p$, and $d$ are the thermal diffusivity, specific heat and sample density, respectively. $D$ was measured by the laser-flash method with a TC1200-RH (Advance Riko) instrument. The $C_p$ value of 0.20 Jg$^{-1}$K$^{-1}$ was obtained from the Dulong–Petit model, $C_p = 3nR$, where $n$ is the number of atoms per formula unit and $R$ is the gas constant. Noted that the actual $C_p$ values of PbTe and PbSe increase few percent at high temperature [33,34], implying that the present $C_p$ value could also be increased few percent at 723 K. Hall coefficient was measured using a physical property measurement system (PPMS, Quantum Design) at room temperature.

**Results and discussion**

Powder XRD patterns for Ag0.25Pb0.50Bi0.25S0.40Se0.50Te0.10 are shown in Figure 1. Although the peaks showed slightly asymmetry, the single-phase and no peak split were observed, indicating the homogeneity of the sample. Note that different compositional ratio of samples resulted in phase separation or inhomogeneity of the composition (Supplemental Fig. S1), thus we report the thermoelectric properties of above compositional sample which showed the best homogeneity. It has been reported that Pb(S/Te) with NaCl type has very low atomic solubility [35]. In this study as well, homogeneity sample was
obtained with a composition in smaller ratio of Te than S, in which S and Te were 40% and 10%, respectively. XRD peaks of the phase can be indexed by the NaCl-type structural model (space group: \textit{Fm\text{3}m}, \#225). Lattice constant is estimated as 5.94858(5) Å. No compositional segregation was detected by EDX mapping (Fig. S2). The average chemical composition of the obtained sample is estimated as Ag\textsubscript{0.257}Pb\textsubscript{0.508}Bi\textsubscript{0.235}S\textsubscript{0.360}Se\textsubscript{0.520}Te\textsubscript{0.120} and concentration was 8.04 \text{mOcm} and 17.3 \text{mOcm} at around 723 K, respectively. To discuss the suppression of \( \rho \) with the actual carrier concentration, Hall effect measurement was performed at room temperature. The Hall coefficient (\( R_{\text{H}} \)) exhibited negative value, indicating the electron carrier is dominant. The estimated carrier concentration was 8.04 \times 10^{19} \text{cm}^{-3}, which is larger than that of 1.44 \times 10^{18} \text{cm}^{-3} for Ag\textsubscript{1/3}Pb\textsubscript{1/3}Bi\textsubscript{1/3}Se, indicating that the suppression of \( \rho \) is caused by increase of carrier concentration possibly due to the deficiency. Considering the increase of electron carrier, the deficiency of chalcogen elements and/or Ag\textsuperscript{1+} is possible. On the other hand, carrier mobility of present sample (\( \mu = 18.52 \text{cm}^{2}\text{V}^{-1}\text{s}^{-1} \)) became lower than that of Ag\textsubscript{1/3}Pb\textsubscript{1/3}Bi\textsubscript{1/3}Se (\( \mu = 273.07 \text{cm}^{2}\text{V}^{-1}\text{s}^{-1} \)). Lowering of mobility can be attributed to the increase of randomness by alloying and/or increase of carrier concentration. A negative value of the S also indicates the n-type polarity of the sample (Figure 2b). The magnitude of the S increased with increasing temperature. Unlike the \( \rho \) behavior, the S exhibited almost same trend as the reference and both values are close.

\[
\Delta S_{\text{mix}}(\text{total}) = \sum_{i=1}^{n} \Delta S_{\text{mix}}^{i}
\]

where \( n \) is the number of crystallographically independent sites in the unit cell. Here, \( \Delta S_{\text{mix}}^{i} \) is calculated by \( \Delta S_{\text{mix}}^{i} = -R \sum_{j=1}^{N} x_{j} \ln x_{j} \), where \( N \) and \( x_{j} \) are number of the component at the mixed site and the atomic fraction of the component, respectively. According to the above formula, present sample possesses \( \Delta S_{\text{mix}}^{\text{cation Site}} = 1.03R \) and \( \Delta S_{\text{mix}}^{\text{anion site}} = 0.96R \), respectively (see inset of Figure 1). Finally, \( \Delta S_{\text{mix}}(\text{total}) = 2.00R \) can be obtained. Let us mention that a similar situation has already been seen for CsCl-type superconductors (Sc,Zr,Nb,Ta)\textsubscript{0.65}(Rh,Pd)\textsubscript{0.35} reported by Stolze et al [36] and NaCl-type MCh [22,28,29]. The obtained \( \Delta S_{\text{mix}} \) exhibited the highest \( \Delta S_{\text{mix}}(\text{total}) \) value among all HEA thermoelectric materials. A schematic image of crystal structure for MCh is shown in inset of Figure 1 together with its mother compound of PbSe.
Figure 2. (a) Temperature dependence of the electrical resistivity and (b) Seebeck coefficient of $\text{Ag}_{0.25}\text{Pb}_{0.50}\text{Bi}_{0.25}\text{S}_{0.40}\text{Se}_{0.50}\text{Te}_{0.10}$ and $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$ as a reference.

Figure 3(a) shows the temperature dependence of $\kappa_{\text{total}}$. Very low $\kappa_{\text{total}}$ of less than 0.75 W m$^{-1}$ K$^{-1}$ is obtained at room temperature, which decreased with heating to 0.61 W m$^{-1}$ K$^{-1}$ at 723 K. The $\kappa_L$ was determined by subtracting the electronic thermal conductivity ($\kappa_e$) from $\kappa_{\text{total}}$ (Figure 4b). $\kappa_e$ was estimated using the following Wiedemann–Franz law, $\kappa_e = LT\rho^{-1}$, where $L$ is the Lorenz number and estimated using an equation $L = 1.5 + \exp(-|S|/116)$ [37]. The value of $\kappa_L$ at room temperature is around 0.62 W m$^{-1}$ K$^{-1}$ and decreased to 0.46 W m$^{-1}$ K$^{-1}$ at $T = 723$ K. Noted that the actual $C_p$ values of PbTe and PbSe increase few percent at high temperature [33,34], implying that the present $C_p$ value could also be increased few percent at 723 K. Contrast to the small temperature dependence of $\kappa_L$ in $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$, the decrease of $\kappa_L$ with increasing temperature indicates that the phonon scattering process is dominated by the Umklapp scattering process. Although the $\kappa_L$ at room temperature showed some difference, they became almost same value at 723 K. In $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$ [11], the fundamental origin of this ultra-low $\kappa_L$ was explained by the synergistic presence of bonding heterogeneity and lattice anharmonicity arising from 6s$^2$ lone pairs of Bi and Pb. They revealed the existence of bonding heterogeneity, which is due to the presence of weak and strong bonding between the Se anion and cation with different electronegativity, using the first-principles density functional theory and electron localization function. In addition, the presence of 6s$^2$ lone pair electrons around Pb and Bi fosters the lattice anharmonicity, which also contributes the reduction of low lattice thermal conductivity. Considering the similarity between the $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$ and present sample, we presumed the ultra-low $\kappa_L$ for present sample is realized by the same situation. Compared to $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$, the present sample exhibited slightly higher lattice thermal conductivity, which is possibly due to the inclusion of lighter element of S with 40% in anion site. Note that, considering the inclusion of both lighter and heavier elements of S with 40% and Te with 10% in anion site, the suppression and enhancement of lowering for thermal conductivity also coexists. This might result in the similar values of $\kappa_L$ between $\text{Ag}_{1/3}\text{Pb}_{1/3}\text{Bi}_{1/3}\text{Se}$ and the present sample. In any case, various synergistic effects, different atomic weight, chemical disorder, solid-solution effect and bonding heterogeneity due to the introduction of MST-HEA would contribute to the suppression of $\kappa_L$. Further investigation for the quantification of the above components and the HEA effect in thermoelectric properties would be required for the development of HEA-type thermoelectric materials, for instance the systematic tuning of atomic weight with same $\Delta S$ value.

Figure 4(a) shows the temperature dependences of the power factor ($S^2\rho^{-1}$). The power factor increases with increasing temperature and reaches the maximum value of 4.4 $\mu$W cm$^{-1}$ K$^{-2}$ at 723 K. The power factor of the sample exhibited over two times higher value within the measured temperature range. Contrast to the close value of $S$ for both results, the around one-third of decrease of $\rho$ for the obtained sample results in the enhancement of power factor. Figure 4(b) shows the temperature dependences of $ZT$. Relatively high $ZT$ value of 0.54 was obtained at 723 K. The $ZT$ value of the present sample exhibited higher than that of the reference at the measured temperature range.
Conclusion

We have synthesized polycrystalline sample of new multi-site-type high-entropy alloyed (MST-HEA) metal chalcogenide Ag$_{0.25}$Pb$_{0.50}$Bi$_{0.25}$S$_{0.40}$Se$_{0.50}$Te$_{0.10}$ with an NaCl-type structure using conventional solid-state reaction. For present sample, $\Delta S_{\text{mix}}$ reached 2.00R, which exceed ideal value of $\Delta S_{\text{mix}} = 1.79R$ for the single-site alloying with six different elements. The concept of MST-HEA in complicated compounds would be useful to develop new HEA-type thermoelectric materials with very high entropy of mixing. The Seebeck coefficient ($S$) and Hall coefficient demonstrated the nature of n-type polarity for the present sample. Compared to the upturn behavior of electrical resistivity ($\rho$) for Ag$_{1/3}$Pb$_{1/3}$Bi$_{1/3}$Se, the $\rho$ linearly increased with increase in temperature for MST-HEA sample and the $\rho$ was suppressed approximately one quarter than that of Ag$_{1/3}$Pb$_{1/3}$Bi$_{1/3}$Se without large decrease of $S$, resulted in the enhancement of power factor. The ultra-low $\kappa_L$ around 0.62 Wm$^{-1}$K$^{-1}$ at room temperature and 0.46 Wm$^{-1}$K$^{-1}$ at $T = 723$ K were achieved possibly due to the synergistic presence of bonding heterogeneity and lattice anharmonicity arising from 6$s^2$ lone pairs of Bi and Pb. The ultra-low $\kappa_L$ and relatively high $ZT$ value suggest that this new MST-HEA MCh could be the promising candidate as an n-type thermoelectric material by further investigation of carrier tuning.

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Disclosure statement
Experimental data are available via reasonable requests to the corresponding author. No potential conflict of interest was reported by the author(s).

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ORCID
Akira Miura http://orcid.org/0000-0003-0388-9696

References
[1] Yang L, Chen ZG, Dargusch MS, et al. High performance thermoelectric materials: progress and their applications. Adv Energy Mater. 2018;8(6):1701797.
[2] Heremans JP, Jovovic V, Toberer ES, et al. Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states. Science. 2008; 321(5888):554–557.
[3] Wang H, Pei Y, LaLonde AD, et al. Heavily doped p-type PbSe with high thermoelectric performance: an alternative for PbTe. Adv Mater. 2011;23(11):1366–1370.
[4] Wang H, Schechtel E, Pei Y, et al. High thermoelectric efficiency of n-type PbS. Adv Energy Mater. 2013;3(4):488–495.
[5] Jood P, Ohta M, Yamamoto A, et al. Excessively doped PbTe with Ge-induced nanostructures enables high-efficiency thermoelectric modules. Joule. 2018;2(7):1339–1355.
[6] Zhang Q, Cao F, Liu W, et al. Heavy doping and band engineering by potassium to improve the thermoelectric figure of merit in p-type PbTe, PbSe, and PbTe$_{1-x}$Se$_x$. J Am Chem Soc. 2012;134(24):10031–10038.
[7] Pei Y, Shi X, LaLonde A, et al. Convergence of electronic bands for high performance bulk thermoelectrics. Nature. 2011;473(7345):66–69.
[8] Wang H, LaLonde AD, Pei Y, et al. The criteria for beneficial disorder in thermoelectric solid solutions. Adv Funct Mater. 2013;23(12):1586–1596.
[9] Yamini SA, Wang H, Gibbs ZM, et al. Chemical composition tuning in quaternary p-type Pb-chalcogenides – a promising strategy for enhanced thermoelectric performance. Phys Chem Chem Phys. 2014;16(5):1835–1840.
[10] Yamini SA, Mitchell DRG, Gibbs ZM, et al. Heterogeneous distribution of sodium for high thermoelectric performance of p-type multiphase lead-chalcogenides. Adv Energy Mater. 2015;5(21):1501047.
[11] Dutta M, Pal K, Waghmare UV, et al. Bonding heterogeneity and lone pair induced anharmonicity resulted in ultralow thermal conductivity and promising thermoelectric properties in n-type AgPbBiSe$_3$. Chem Sci. 2019;10:4905–4913.
[12] Yeh JW, Chen SK, Lin SJ, et al. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. Adv Eng Mater. 2004;6:299–303.
[13] Tsai MH, Yeh JW. High-entropy alloys: A critical review. Mater Res Lett. 2014;2(3):107–123.
[14] Kitagawa J, Hamamoto S, Ishizu N. Cutting edge of high-entropy alloy superconductors from the perspective of materials research. Metals (Basel). 2020;8:1078.
[15] Sogabe R, Goto Y, Mizuguchi Y. Superconductivity in RE$_{0.5}$F$_{0.5}$Bi$_2$S$_2$ with high-entropy-alloy-type blocking layers. Appl Phys Express. 2018;11:053102.
[16] Sogabe R, Goto Y, Abe T, et al. Improvement of superconducting properties by high mixing entropy at blocking layers in Bi$_2$-based superconductor RE$_{0.5}$F$_{0.5}$Bi$_2$S$_2$. Solid State Commun. 2019;295:43–49.
[17] Mizuguchi Y. Superconductivity in high-entropy-alloy telluride AgInSnPbBiTe$_3$. J Phys Soc Jpn. 2019;88:124708.
[18] MdR K, Hoshi K, Jha R, et al. Superconducting properties of high-entropy-alloy tellurides M-Te (M: Ag, In, Cd, Sn, Sb, Pb, Bi) with a NaCl-type structure. Appl Phys Express. 2020;13(3):033001.
[19] Shukunami Y, Yamashita A, Goto Y, et al. Synthesis of RE123 high-T$_c$ superconductors with a high-entropy-alloy-type RE site. Physica C. 2020;153623.
[20] Yamashita A, Jha R, Goto Y, et al. An efficient way of increasing the total entropy of mixing in high-entropy-alloy compounds: a case of NaCl-type (Ag,In,Pb,Bi)Te$_{1-x}$Se$_x$ (x = 0.0, 0.25, 0.5) superconductors. Dalton Trans. 2020;49:9118–9122.
[21] Mizuguchi Y, Kasem M, Matsuda TD. Superconductivity in CuAl$_{1-x}$Co$_x$Ni$_2$Sn$_3$ with a high-entropy-alloy-type blocking layer in Bi$_2$-based superconductor RE$_{0.5}$F$_{0.5}$Bi$_2$S$_2$ with high-entropy-alloy transition metal site. Mater Res Lett. 2020;9(3):141–147.
[22] Kasem MR, Yamashita A, Goto Y, et al. Synthesis of high-entropy-alloy-type superconductors (Fe,Co,Ni,Rh,Ir)Zr$_2$ with tunable transition temperature. arXiv:2011.05590.
[23] Shuai J, Mao J, Song S, et al. Recent progress and future challenges on thermoelectric zintl materials. Mater Today Phys. 2017;1:74–95.
[24] Zhang Y, Zuo TT, Tang Z, et al. Microstructures and properties of high-entropy alloys. Prog Mater Sci. 2014;61:1–93.
[25] Shaleie S. High-entropy alloys as high-temperature thermoelectric materials. J Appl Phys. 2015;118(184905):1–10.
[26] Yan J, Liu F, Ma G, et al. Suppression of the lattice thermal conductivity in NbFeSb-based half-Heusler thermoelectric materials through high entropy effects. Scr Mater. 2018;157:129–134.
[27] Karati A, Nagini M, Ghosh S, et al. Ti$_2$NiCoSnSb - a promising strategy for enhanced thermoelectric performance in CuAl$_2$-type Co$_{0.2}$Ni$_{0.1}$Cu$_{0.1}$Rh$_{0.3}$Ir$_{0.3}$Zr$_2$ with tunable transition temperature. arXiv:2011.05590.
[28] Liu F, Wang J, Gao X, et al. High-entropy-alloy-type superconductors with a high-entropy-alloy-type RE site. Physica C. 2020;153623.
[29] MdR K, Hoshi K, Jha R, et al. Superconducting properties of high-entropy-alloy tellurides M-Te (M: Ag, In, Cd, Sn, Sb, Pb, Bi) with a NaCl-type structure. Appl Phys Express. 2020;13(3):033001.
[31] Izumi F, Momma K. Three-dimensional visualization in powder diffraction. Solid State Phenom. 2007;130:15–20.

[32] Momma K, Izumi F. VESTA: a three-dimensional visualization system for electronic and structural analysis. J Appl Crystallogr. 2008;41:653–658.

[33] Zhou M, Li J-F, Kita T. Nanostructured AgPb$_{m}$SbTe$_{m+2}$ system bulk materials with enhanced thermoelectric performance. J Am Chem Soc. 2008;130(13):4527–4532.

[34] Huang Z, Wang D, Li C, et al. Improving the thermoelectric performance of p-type PbSe via synergistically enhancing the Seebeck coefficient and reducing electronic thermal conductivity. J Mater Chem A. 2020;8(9):4931–4937.

[35] Liu R, Chen H, Zhao K, et al. Entropy as a gene-like Performance indicator promoting thermoelectric materials. Adv Mater. 2017;29:1702712–1702718.

[36] Stolze K, Tao J, von Rohr FO, et al. Sc–Zr–Nb–Rh–Pd and Sc–Zr–Nb–Ta–Rh–Pd high-entropy alloy superconductors on a CsCl-type lattice. Chem Mater. 2018;30:906–914.

[37] Kim H-S, Gibbs ZM, Tang Y, et al. Characterization of Lorenz number with Seebeck coefficient measurement. APL Mater. 2015;3:041506–04041510.