Bipolar doping and thermoelectric properties of Zintl arsenide Eu₅In₂As₆

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Zintl compounds exhibit promising thermoelectric properties because of the feasibility of the chemical tuning of their electrical and thermal transport. While most Zintl pnictides are known to show p-type polarity, recent developments in high-performance n-type Mg₃Sb₂-based thermoelectric materials have encouraged further identification of n-type Zintl pnictides. In this study, we demonstrate the bipolar dopability of the Zintl arsenide Eu₅In₂As₆. The electrical resistivity at 300 K with n-type polarity was decreased to 7.6 × 10⁻¹ Ωcm using La as an electron dopant. In contrast to the relatively high resistivity of n-type Eu₅In₂As₆, the p-type resistivity at 300 K was decreased to 5.9 × 10⁻³ Ωcm with a carrier concentration of 2.8 × 10²⁰ /cm³ using Zn as a hole dopant. This doping asymmetry is discussed in terms of the weighted mobility of electrons and holes. Furthermore, a very low lattice thermal conductivity of 0.7 W/mK was observed at 773 K, which is comparable to that of the Sb-containing analogue Eu₅In₃Sb₂. The dimensionless figure of merit ZT = 0.29 at 773 K for Zn-doped p-type Eu₅In₂As₆. This study shows that bipolar dopable Eu₅In₂As₆ can be a platform to facilitate a better understanding of the doping asymmetry in Zintl pnictides.

1. Introduction

Controlling the charge carrier polarity and concentration is essential for the development of novel semiconductor devices. For example, the thermoelectric module enables interconversion between temperature difference and electricity, and is a promising component for energy harvesting from waste heat.¹⁻⁴ The conventional thermoelectric module requires the integration of p-type and n-type semiconductors. The performance of thermoelectric materials is characterised by a dimensionless figure of merit, ZT = S²T /ρκ, where T is the absolute temperature, S is the Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity. Therefore, both p-type and n-type semiconductors that show high ZT values are required to construct efficient thermoelectric modules.

Various thermoelectric materials have been investigated over the past several decades. Among them, Zintl phase pnictides, which consist of covalently bonded anionic frameworks and cations, have been studied extensively because of their fascinating compositional/structural varieties and promising thermoelectric properties.⁵⁻⁷ For example, AB₃X₇, A₆BₓX₇₋ₓ, A₆BₓX₈, A₆BₓAsₓX₈₋ₓ, and A₆BX₇—where A denotes an alkali/alkaline-earth/rare-earth metal, B is a (post-) transition metal, and X is a pnictogen—have been demonstrated as promising thermoelectric materials.⁸⁻¹⁵ owing to the complex crystal structure that can lead to intrinsically lattice thermal conductivity, while the presence of covalent bonding maintains moderately high carrier mobility. Such characteristics offer promise for efficient thermoelectric devices as well as other state-of-the-art thermoelectric materials, including GeTe,¹⁶⁻¹⁷ SnSe,¹⁸ SnTe,¹⁹ flexible materials,²⁰ oxides,²¹ etc.

While most Zintl pnictides are known to show p-type polarity, the recent development of high-performance n-type Mg₃Sb₂-based thermoelectric materials, which exhibit ZT = 1.51 at 716 K,¹³,¹⁴ has encouraged further identification of n-type Zintl pnictides. However, fabricating n-type Zintl pnictides is not an easy task because most of the n-type doping is compensated by the so-called killer defects, such as cation vacancies.²² In addition to Mg₃Sb₂-based materials, AB₆X₇,²³,²⁴ Eu₅InₓLaₓIn₃Sb₂,²⁵ Eu₅In₃Sb₂,²⁶ and Ba₃Cd₂P₂,²⁷ have been reported as n-type Zintl pnictides so far.

The crystal structure of Zintl arsenide Eu₅In₂As₆ belongs to the orthorhombic space group Pbam, as shown in Figure 1.²⁸,²⁹ Each In atom is four-fold coordinated by As atoms to form InAs₄ tetrahedra, which are corner-shared along the c axis. The chains of InAs₄ tetrahedra are further bridged by As–As bonds. The Eu atoms between the chains provide electrons to the covalently bonded anionic framework, yielding an overall charge balance. Mössbauer spectroscopy suggests the valence state as Eu⁺⁺⁺In⁺⁺⁺As⁺⁺⁺As⁺⁺⁺, while Zintl-concept describes that as Eu⁺⁺⁺In⁺⁺⁺As⁺⁺⁺As⁺⁺⁺. This material undergoes two-step magnetic transitions at 5 K and 16 K, likely because of Eu⁺⁺⁺ ions that include three distinct crystallographic sites.²⁹

In this study, we demonstrate that Zintl arsenide Eu₅In₂As₆ is a bipolar dopable material. La and Zn were used as the n-type and p-type dopants, respectively, because these elements have been
investigated as effective dopants in the sister compound Eu₅InSb₆. While n-type Eu₅InAs₆ shows relatively high electrical resistivity of \( \sim 10^{-4} \) Ωcm, p-type samples exhibit resistivity as low as \( \sim 10^{-3} \) Ωcm. This doping asymmetry is discussed in terms of the weighted mobility of electrons and holes. Furthermore, a very low lattice thermal conductivity of 0.7 W/mK was observed at 773 K. First-principles calculations were performed to investigate the electronic structure and transport properties.

2. Method

Sample preparation

Polycrystalline Eu₅InAs₆ was prepared by reacting EuAs, InAs, and In (99.99%) powder, which is similar to the method employed in our previous studies. EuAs was prepared by reacting Eu (99.9%) with As (99.9999%) in a 1:1 stoichiometric ratio at 850 °C for 10 h in a carbonised silica tube. We scraped the surface of the Eu ingot mechanically by filing it before use. We then cut or crushed the Eu ingot and As grains into small pieces to ensure the feasibility of the reaction by increasing the surface area. The silica tube was carbonised via the evaporation of acetone. InAs was prepared by reacting In with As in a 1:1 stoichiometric ratio at 950 °C for 10 h in a sealed silica tube. We then prepared a stoichiometric mixture of EuAs, InAs, and In in a 1:1:1 ratio, which was then pelletised, placed in a carbon crucible, and heated at 800 °C for 30 h in a sealed silica tube. We also prepared Eu₅₋ₓLaₓInₓAs₆ (x = 0.05, 0.10) and Eu₅Inₓ₋₂ZnₓAs₆ (y = 0.05, 0.10, and 0.15). LaAs was added to the precursor for the synthesis of Eu₅₋ₓLaₓInₓAs₆. LaAs was prepared by reacting La (99.9%) with As in a 1:1 stoichiometric ratio at 700 °C for 20 h in a silica tube. For the synthesis of Eu₅Inₓ₋₂ZnₓAs₆, Zn (99.9%) was added to the precursor.

We compressed the obtained samples by hot-pressing them in a graphite die at 50 MPa and 650–700 °C for 30 min. We calculated the geometric density of each sample to be >95% of the corresponding unit cell density. The obtained samples were observed to endure at least several weeks of exposure to air without visible signs of oxidation/hydrolysis.

Sample characterisation

We examined particle size and morphology of the obtained samples using scanning electron microscopy (SEM; Hitachi TM3030). We investigated the chemical compositions using energy-dispersive X-ray spectrometry (EDX; Oxford SwiftED3000). We measured the X-ray diffraction (XRD) patterns in the laboratory with CuKα radiation using a Rigaku MiniFlex 600 equipped with a D/teX Ultra detector. In addition, we measured the SXRD patterns at BL02B2 of SPring-8 under proposal number 2021A1573. The diffraction data were obtained using a high-resolution one-dimensional semiconductor detector (MYTHEN). The wavelength of the radiation beam was determined to be 0.495810(1) Å using a CeO₂ standard. The crystal structure parameters were refined by the Rietveld method using JANA 2020 using the diffraction intensity data in the reciprocal space of \( \sin \theta / \lambda < 0.52 / \text{Å} \) (lattice spacing \( d > 0.96 \) Å). The crystal structure was visualised using VESTA.

Thermoelectric transport properties

We measured the Hall coefficient \( R_H \) using the five-probe method with a physical property measurement system (Quantum Design). We calculated the Hall carrier concentration as \( n_H = 1/R_H e \), where \( e \) is the charge of an electron. We measured the electrical resistivity and Seebeck coefficient using a four-probe method and a quasi-steady-state method, respectively (ZEM-3, Advance Riko). The thermal diffusivity was measured using a laser flash method (TC-1200RH, Advance Riko). We calculated the thermal conductivity using the relationship \( \kappa = DC_d/\rho \), where \( D \), \( C_p \), and \( d \) are the thermal diffusivity, specific heat, and sample density, respectively. We estimated \( C_p \) using the Dulong–Petit law, \( C_p = 3n_e R \), where \( n_s \) is the number of atoms per formula unit, and \( R \) is the gas constant.

The thermal hysteresis of the samples used in this study is almost negligible, at least up to 773 K.

First-principles calculation

We performed first-principles calculations within density functional theory (DFT) using VASP 5.4.4 to obtain the electronic structure of Eu₅InAs₆ by adopting the experimentally determined structural parameters. We calculated the electronic density, including spin–orbit coupling, self-consistently with the modified Becke–Johnson potential using a 3 × 3 × 8 k-mesh. The cut-off energy for the plane-wave basis set was fixed at 350 eV. For Eu, we used the potentials obtained with open-core treatment for the f-electrons. We calculated the Seebeck coefficient within the Boltzmann transport theory, as implemented in the BoltzTraP code using an 11 × 10 × 29 k-mesh. We assumed the rigid-band approximation and a constant relaxation time to calculate the Seebeck coefficient tensors. For a comparison with the experimental results for polycrystalline samples, we obtained the final results for the Seebeck coefficients by averaging the xx, yy, and zz components of the Seebeck coefficient tensor.

3. Results

Sample characterisation

The chemical compositions determined using EDX are summarised in Table 1. The analysed composition is reasonably consistent with the nominal composition of the starting materials. SEM images show that the obtained samples are µm-sized particles, as shown in Figure S1.
doping may be compensated (different in La$_{0.6}$ and than that of In-content, which is consistent with the smaller ionic radius of Zn.

The lattice parameters are consistent with previously reported results. Eu$_{1-y}$La$_y$In$_{1-x}$As$_x$ and Eu$_{1-y}$Zn$_y$As$_x$.

Table 1 Chemical compositions obtained using EDX and the lattice parameters of Eu$_{1-y}$La$_y$In$_{1-x}$As$_x$ and Eu$_{1-y}$Zn$_y$As$_x$.

| Nominal composition | Analysed composition | Lattice parameters |
|---------------------|----------------------|--------------------|
| Eu$_{1-y}$La$_y$In$_{1-x}$As$_x$ | Eu:La:In:As | a (Å) | b (Å) | c (Å) | V (Å$^3$) |
| x = 0 | 4.7(2):0.2:0.4(6):6.3(3) | 11.89005(4) | 13.79079(4) | 4.35060(13) | 713.38(4) |
| 0.05 | 4.69(5):0.01(1):2.03(5):6.27(7) | 11.88898(7) | 13.79239(8) | 4.35021(2) | 713.36(7) |
| 0.10 | 4.57(7):0.03(2):2.04(4):6.4(1) | 11.88856(15) | 13.79437(17) | 4.35080(5) | 713.51(2) |
| Eu$_{1-y}$Zn$_y$As$_x$ | Eu:In:Zn:As | y = 0.05 | 4.6(1):1.99(4):0.01(1):6.4(1) | 11.89106(6) | 13.78907(8) | 4.34756(2) | 712.85(6) |
| 0.10 | 4.65(8):1.98(5):0.03(2):6.4(1) | 11.89062(6) | 13.78546(7) | 4.34384(2) | 712.03(6) |
| 0.15 | 4.6(1):2.0(1):0.04(3):6.2(2) | 11.89168(19) | 13.7879(2) | 4.34427(7) | 712.29(2) |

- Lattice parameters of y = 0.15 was obtained using laboratory XRD measurements.

Figure 2 shows the SXRD pattern of Eu$_{1-y}$La$_y$In$_{1-x}$As$_x$ and the Rietveld refinement results. The circles (red) and solid lines (black) represent the observed and calculated patterns, respectively. The difference between the observed and calculated patterns is shown at the bottom (blue). The vertical marks indicate the Bragg reflection positions for Eu$_{1-y}$La$_y$In$_{1-x}$As$_x$, Eu$_{1-y}$As$_x$, and Eu$_{1-y}$O$_x$, respectively, from top to bottom. The reliability factors are $R_{Bragg} = 8.35\%$, $R_B = 6.78\%$, and $GOF = 9.70$. Analogous data for other samples are shown in Figure S2 in ESI.

The Rietveld refinement of site occupancy gives In : Zn = 0.97 : 0.03 for Eu$_{1-y}$La$_y$Zn$_{1-x}$As$_x$, indicating that Zn dopants indeed occupy the In site. Although we performed site occupancy analysis for La-doped samples, it is difficult to obtain reasonable results, likely because of similar electron numbers of Eu and La. The Rietveld refinement results for the other samples are shown in Figure S2 and Table S1 in ESI. Hereafter, we denote the samples using the nominal composition of the starting materials for simplicity.

**Charge-carrier transport**

Figure 3 shows the electrical resistivity and Seebeck coefficient at 300 K. The electrical resistivity of undoped Eu$_{1-y}$In$_{1-x}$As$_x$ is 7.2 $\Omega$cm, which is decreased by La or Zn doping; the corresponding values for Eu$_{1-y}$La$_y$In$_{1-x}$As$_x$ and Eu$_{1-y}$Zn$_{1-x}$As$_x$ are 7.6 $\times$ 10$^{-3}$ $\Omega$cm and 5.9 $\times$ 10$^{-3}$ $\Omega$cm, respectively. Thus, Zn is a more effective dopant for inducing carriers in Eu$_{1-y}$In$_{1-x}$As$_x$. The Seebeck coefficient of the undoped sample is $\sim$32 $\mu$V/K, that is, undoped Eu$_{1-y}$In$_{1-x}$As$_x$ already exhibits n-type polarity, because the sign of the Seebeck coefficient is a measure of the carrier polarity. This is in contrast to the p-type polarity of most Zn-doped pnictides. Despite the high resistivity of the undoped sample (7.2 $\Omega$cm), the absolute value of the Seebeck coefficient was not significantly high. This is likely because of the multicarrier nature of the undoped sample, namely, the coexistence of electrons and holes, which is also suggested by the temperature dependence of the Seebeck coefficient, as shown later. The Seebeck coefficient of the La/Zn-doped samples shows a negative/positive sign. The results indicate that La/Zn acts as an electron/hole dopant in Eu$_{1-y}$In$_{1-x}$As$_x$, as expected from the simple ionic valence counting (La$^{3+}$:doping into Eu$^{3+}$, and Zn$^{2+}$:doping into In$^{3+}$). For the Zn-doped sample, the Seebeck coefficient decreased to 96 $\mu$V/K, which is consistent with the decrease in electrical resistivity.

The Hall coefficient of undoped Eu$_{1-y}$In$_{1-x}$As$_x$ was measured to be $\sim$35.4 cm$^3$/C. The negative sign of the Hall coefficient confirms the n-type polarity of Eu$_{1-y}$In$_{1-x}$As$_x$, which is consistent with the Seebeck coefficient. The Hall carrier concentration of Eu$_{1-y}$In$_{1-x}$As$_x$ was determined to be $1.8 \times 10^{17}$/cm$^3$, and it increased with increasing Zn content. As shown in Figure 4, an increase in carrier concentration with Zn content is reasonably consistent with the expected value, assuming that each Zn generates one free hole, although the experimental carrier concentration is slightly lower than the expected value. Unlike for the Zn-doped samples, it is
difficult to obtain reliable Hall coefficients of the La-doped samples, probably because of their low electron mobility. To discuss the mobility of these samples, we calculated the weighted mobility $\mu_w$, that is, the carrier mobility weighted by the density of electronic states, using their electrical resistivity and Seebeck coefficient. It has been reported that the weighted mobility provides a reasonable assessment of carrier mobility even if the materials have a low mobility. As listed in Table 2, the magnitude of the weighted mobility of the Zn-doped samples was $\sim 10^{-1}$ cm$^2$/Vs, whereas that of the La-doped samples was $\sim 10^{-1}$ cm$^2$/Vs. These results confirm the difficulty in measuring the Hall coefficient of La-doped samples due to low electron mobility. We estimated Hall coefficient of La-doped samples at 0.5 cm$^3$/C (Eu$_{4.95}$La$_{0.05}$In$_2$As$_6$) and 1.3 cm$^3$/C (Eu$_{4.80}$La$_{0.10}$In$_2$As$_6$), using measured electrical resistivity and calculated weighted mobility. However, these values might be overestimated because weighted mobility tends to be higher than Hall mobility (Table 2).

Fig. 3 (a) Electrical resistivity $\rho$ and (b) Seebeck coefficient $S$ of Eu$_{5-x}$La$_x$In$_2$As$_6$ and Eu$_{5}$In$_2$Zn$_y$As$_6$ at 300 K.

Fig. 4 Hall carrier concentration of Eu$_{5}$In$_2$Zn$_y$As$_6$ at 300 K. The dashed line represents the expected value, assuming each Zn provides one free hole.

Fig. 5 Electrical resistivity $\rho$, Seebeck coefficient $S$, and electrical power factor PF as functions of temperature $T$ for Eu$_{5-x}$La$_x$In$_2$As$_6$ and Eu$_{5}$In$_2$Zn$_y$As$_6$.
comparable to that of the Sb-doped samples exhibit a power factor of approximately 0.3
than 0.2 mW/mK increasing temperature without a maximum.

The Seebeck coefficient of the Zn exhibit a maximum at approximately 570 K. In contrast, the
Seebeck coefficient decreases with increasing temperature above this temperature, indicating the multicarrier nature of undoped 
Eu.

Although the electrical resistivity of the La-doped samples is decreased, their semiconducting behaviour is still maintained. In contrast, degenerate conduction (positive temperature coefficient) is observed for the Zn-doped samples.

The Seebeck coefficient of the undoped sample shows a maximum at approximately 420 K, and the absolute value of the Seebeck coefficient decreases with increasing temperature above this temperature, indicating the multicarrier nature of undoped EuInAs. This is consistent with its low electron mobility, as listed in Table 2. The Seebeck coefficient of the La-doped samples still exhibits a maximum at approximately 570 K. In contrast, the Seebeck coefficient of the Zn-doped samples increases with increasing temperature without a maximum.

The calculated power factor of the La-doped samples is less than 0.2 mW/mK because of their high electrical resistivity. The Zndoped samples exhibit a power factor of approximately 0.3 mW/mK over a broad temperature range (500–800 K), which is comparable to that of the Sb-containing analogue EuInSb.S.

Table 2 Hall carrier concentration \( n_h \), Hall carrier mobility \( \mu_h \), and weighted mobility \( \mu_w \) for EuInAs and EuIn2–ZnAs at 300 K. A reliable Hall coefficient was not obtained for EuIn2–LaAs (\( x = 0.05 \) and 0.10).

| Sample         | \( n_h \) (cm\(^{-3}\)) | \( \mu_h \) (cm\(^2\)/Vs) | \( \mu_w \) (cm\(^2\)/Vs) |
|----------------|-------------------------|---------------------------|---------------------------|
| EuIn2–LaAs     | \( x = 0 \)             | 1.8 \times 10^{17}        | 4.9                       |
|                | \( 0.05 \)               | —                         | 6.1 \times 10^{-1}       |
|                | \( 0.10 \)               | —                         | 9.4 \times 10^{-1}       |
| EuIn2–ZnAs     | \( y = 0.05 \)           | 1.1 \times 10^{20}        | 3.7                       |
|                | \( 0.10 \)               | 1.9 \times 10^{20}        | 4.7                       |
|                | \( 0.15 \)               | 2.8 \times 10^{20}        | 3.8                       |
|                |                         |                           | 21.6                      |

Figure 6 shows the temperature dependence of the electrical resistivity, Seebeck coefficient, and power factor \( (PF = \rho^{-1}S^2) \) of EuInAs and EuIn2–ZnAs. The undoped sample shows a semiconducting behaviour with high resistivity, and the activation energy is evaluated to be 0.29 eV using the Arrhenius plot \( \ln(\rho) \) vs. \( T^{-1} \) in the high-temperature region, as shown in Figure S3. Although the electrical resistivity of the La-doped samples is decreased, their semiconducting behaviour is still maintained. In contrast, degenerate conduction (positive temperature coefficient) is observed for the Zn-doped samples.

The Seebeck coefficient of the undoped sample shows a maximum at approximately 420 K, and the absolute value of the Seebeck coefficient decreases with increasing temperature above this temperature, indicating the multicarrier nature of undoped EuInAs. This is consistent with its low electron mobility, as listed in Table 2. The Seebeck coefficient of the La-doped samples still exhibits a maximum at approximately 570 K. In contrast, the Seebeck coefficient of the Zn-doped samples increases with increasing temperature without a maximum.

The calculated power factor of the La-doped samples is less than 0.2 mW/mK because of their high electrical resistivity. The Zn-doped samples exhibit a power factor of approximately 0.3 mW/mK over a broad temperature range (500–800 K), which is comparable to that of the Sb-containing analogue EuInSb.30

Figure 6(a) shows the thermal conductivity as a function of the temperature. The thermal conductivity of undoped EuInAs is 1.6 W/mK at 300 K. Furthermore, it decreases monotonically with increasing temperature, likely due to the Umklapp scattering of phonons, and becomes 0.9 W/mK at 673 K. All the examined samples show comparable thermal conductivities. However, the Zn-doped samples show a slightly high thermal conductivity because of the increased carrier contribution. The total thermal conductivity consists of the lattice and carrier contributions. The carrier contribution to thermal conductivity is estimated using the Wiedemann–Franz relationship, \( \kappa_{\text{el}} = L T \rho^{-1} \), where \( L \) is the Lorentz number. We calculated \( L \) using the formula \( L = 1.5 + \exp(S/116) \), where \( L \) and \( S \) are in units of \( 10^{-8} \) W/ΩK\(^2\) and µV/K, respectively. We obtained the lattice thermal conductivity by subtracting the electronic component from the total thermal conductivity. As shown in Figure 6(b), the lattice thermal conductivities of these samples are within the experimental uncertainty, which is roughly estimated to be 10%.

It is interesting to note that bipolar contribution to carrier thermal conductivity seems to be negligibly small, unlike

\( \text{Fig. 6} \) Temperature (\( T \)) dependence of the (a) total thermal conductivity \( \kappa \) and (b) lattice thermal conductivity \( \kappa_l \) of EuInAs and EuIn2–ZnAs.

\( \text{Fig. 7} \) Dimensionless figure of merit \( ZT \) as a function of temperature \( T \) for EuInAs and EuIn2–ZnAs.

\( \text{Table 2} \) Hall carrier concentration \( n_h \), Hall carrier mobility \( \mu_h \), and weighted mobility \( \mu_w \) for EuInAs and EuIn2–ZnAs at 300 K. A reliable Hall coefficient was not obtained for EuIn2–LaAs (\( x = 0.05 \) and 0.10).

\( \text{Fig. 8} \) Band structure and density of states (DOS) of EuInAs. Horizontal dashed lines in band structure indicate the Fermi level of respective electron concentration \( (n_e) \) and hole concentration \( (n_h) \).
The temperature dependence of Seebeck coefficient shows the contribution from minority carriers. In a two-carrier model, Seebeck coefficient and bipolar thermal conductivity \( \kappa_{\text{bip}} \) are expressed as follows:

\[
S = \frac{S_h \sigma_h + S_e \sigma_e}{\sigma_h + \sigma_e},
\]

\[
\kappa_{\text{bip}} = (S_h - S_e)^2 \frac{\sigma_h \sigma_e T}{(\sigma_h + \sigma_e)^2},
\]

where \( S_h, S_e, \sigma_h, \) and \( \sigma_e \) are hole Seebeck coefficient, electron Seebeck coefficient, hole electrical conductivity, and electron electrical conductivity, respectively. Therefore, negligible small bipolar thermal conductivity in Eu\(_{1-n}\)In\(_n\)As\(_6\) is most likely due to low \( \sigma_h \) and \( \sigma_e \).

Furthermore, the lattice thermal conductivity of these samples is comparable to that of the Sb-containing analogue Eu\(_{1-n}\)In\(_n\)Sb\(_6\). This suggests that the low thermal conductivity originates from structural complexity and/or bonding anharmonicity, rather than the heavy constituent elements. For example, a crystal structure characterised by a quasi-one-dimensional chain of InAs\(_6\) tetrahedra may contribute to low thermal conductivity. However, a detailed investigation of phonon properties, such as first-principles calculation of phonon dynamics, is required for a further analysis of this phenomenon.

Figure 7 shows the calculated ZT values for Eu\(_{1-n}\)La\(_n\)In\(_2\)As\(_6\) and Eu\(_{1-n}\)Zn\(_n\)As\(_6\). The value of ZT for Eu\(_{1-n}\)La\(_n\)In\(_2\)As\(_6\) is less than 0.1, whereas it reaches 0.29 at 773 K for Eu\(_{1-n}\)Zn\(_n\)As\(_6\). This is mainly because of the sufficient carrier doping in these samples, as described above.

**First-principles calculation**

The first-principles calculations show that Eu\(_{1-n}\)In\(_n\)As\(_6\) has a semiconducting band structure, as shown in Figure 8. The band gap is evaluated to be 0.7 eV, which is reasonably consistent with the value experimentally obtained using the temperature dependence of electrical resistivity, 0.58 eV. Both the valence band maximum (VBM) and conduction band minimum (CBM) are located on the Y–Γ line. The density of states (DOS) of the VBM has a higher value than that of the CBM. As shown in Figure 53, the VBM is predominantly composed of the As 4p orbital, whereas the CBM is composed of In 5s/5p, As 4p, and Eu 5d orbitals. We also calculated band structure of Zn-doped Eu\(_{1-n}\)In\(_n\)As\(_6\) using virtual crystal approximation. However, the obtained band structure almost coincides with undoped Eu\(_{1-n}\)In\(_n\)As\(_6\), except for the Fermi level (results are not shown), indicating that rigid band model can be accepted to investigate the carrier transport of these compounds.

The hole concentration dependence of the calculated and measured Seebeck coefficients is shown in Figure 9(a). Here, we show the results of Eu\(_{1-n}\)Zn\(_n\)As\(_6\) with p-type polarity, because the Hall coefficient was successfully obtained for these samples. The calculated results using DFT are reasonably consistent with the experimental results, although the calculations slightly underestimate the experimental results. We also show the Seebeck coefficient obtained using a single parabolic band (SPB) model with acoustic phonon scattering. The measured Seebeck coefficient is well reproduced with an effective mass of 2.2 \( m_0 \), which is the rest mass of a free electron. It should be noted that effective mass of undoped Eu\(_{1-n}\)In\(_n\)As\(_6\) is apparently lower than that of Zn-doped samples. This is because the effective mass analysis using Seebeck coefficient and carrier concentration assumes single parabolic band, while temperature dependence of Seebeck coefficient of undoped Eu\(_{1-n}\)In\(_n\)As\(_6\) indicates that this should be regarded as a multicondition system.

Figure 9(b) shows the Seebeck coefficient obtained using the first-principles calculations for the p-type and n-type polarity. A higher Seebeck coefficient is obtained for p-type polarity, which is consistent with the higher DOS near the VBM than that near the CBM, as shown in Figure 8.

The calculated temperature dependence of the Seebeck coefficient is shown in Figure 55. For the p-type region, the Seebeck coefficient increases with increasing temperature, which is consistent with the experimental results. On the other hand, the calculated Seebeck coefficient in the n-type region also increases almost monotonically with increasing temperature, unlike experiments that show a maximum in the mid-temperature region (Fig. 5). This is likely because of the asymmetry in the relaxation times of electrons and holes, which is assumed to be constant in the theoretical calculation. The asymmetry in the carrier relaxation time is also suggested by the large difference in the weighted mobilities of the p-type and n-type samples, as listed in Table 2.

**4. Discussion**

In the present study, it was shown that Zn acts as an efficient dopant to induce hole carriers. In contrast, electron doping using La as the dopant appears to be compensated by defects, such as cation (Eu and/or In) vacancies. In some Zintl compounds, it has been demonstrated that excess amounts of cations are effective in suppressing cation vacancies, which is conceptualised by the so-called phase boundary mapping. We preliminarily investigated the synthesis of La-doped Eu\(_{1-n}\)In\(_n\)As\(_6\) with excess amounts of Eu or In. Regrettably, these samples show almost comparable thermoelectric transport to those of stoichiometric compounds without excess cations, suggesting that dopant activity is difficult to control via non-stoichiometry.
5. Conclusions

We demonstrated Zintl arsenide Eu$_5$In$_2$As$_6$ as a bipolar dopable material. The n-type polarity was confirmed in La-doped Eu$_5$In$_2$As$_6$, although the electron concentration was shown to be lower than the optimal value as indicated from high electrical resistivity. The p-type polarity was observed in the Zn-doped samples, and the hole concentration was optimised, leading to $ZT = 0.29$ at 773 K. This doping asymmetry is understood by the difference in the weighted mobility of electrons and holes. The bipolar dopable Eu$_5$In$_2$As$_6$ will be a useful platform to facilitate a better understanding of the doping asymmetry in Zintl pnictides.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partly supported by The Iwataki Naoji Foundation (20-4725), JST CREST (No. JPMJCR16Q6), JSPS KAKENHI (No. 19K15291, 19K15436, 20KK0124), and Tokyo Metropolitan Government Advanced Research (H31-1).

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Electronic Supplementary Information for

Bipolar doping and thermoelectric properties of Zintl arsenide

\( \text{Eu}_5\text{In}_2\text{As}_6 \)

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Figure S1. SEM images of pulverized powder of (a) Eu$_5$In$_2$As$_6$, (b) Eu$_{4.90}$La$_{0.10}$In$_2$As$_6$, and (c) Eu$_5$In$_{1.90}$Zn$_{0.10}$As$_6$.

Figure S2
Observed synchrotron X-ray diffraction pattern and the Rietveld refinement results. The circles (red) and solid lines (black) represent the observed and calculated patterns, respectively. The difference between the observed and calculated patterns is shown at the bottom (blue). The vertical marks indicate the Bragg reflection positions for Eu$_3$In$_2$As$_6$-type phase, Eu$_3$In$_2$As$_4$, and Eu$_2$O$_3$, respectively, from top to bottom. Amount of these phases are denoted in the inset.
Table S1
Reliability factors of the Rietveld refinement of $\text{Eu}_{5-x}\text{La}_x\text{In}_2\text{As}_6$ and $\text{Eu}_5\text{In}_{2-y}\text{Zn}_y\text{As}_6$.

| Sample            | $R_{wp}$ (%) | $R_p$ (%) | GOF   |
|-------------------|--------------|-----------|-------|
| $\text{Eu}_{5-x}\text{La}_x\text{In}_2\text{As}_6$ |              |           |       |
| $x = 0$           | 5.37         | 5.17      | 7.17  |
| 0.05              | 8.70         | 7.92      | 11.17 |
| 0.10              | 8.35         | 6.78      | 9.70  |
| $\text{Eu}_5\text{In}_{2-y}\text{Zn}_y\text{As}_6$ |              |           |       |
| $y = 0.05$        | 5.58         | 5.77      | 7.93  |
| 0.10              | 6.94         | 6.97      | 9.80  |

Figure S3
Temperature ($T$) dependence of electrical resistivity ($\rho$) of $\text{Eu}_5\text{In}_2\text{As}_6$. Activation energy ($E_a$) was obtained using measurement results from 623 to 778 K.
Figure S4
Partial density of states (DOS) of EuIn₂As₆.
Figure S5
Temperature ($T$) dependence of Seebeck coefficient ($S$) of Eu$_5$In$_{1.95}$Zn$_{0.05}$As$_6$ and Eu$_{4.90}$La$_{0.10}$In$_2$As$_6$. Calculated $S$ using density functional theory (DFT) is also shown. Measured hole concentration ($1.1 \times 10^{20}$ cm$^{-3}$) was used to plot calculated results for p-type region, while electron concentration of $1.6 \times 10^{19}$ cm$^{-3}$ was assumed for n-type region, because reliable Hall coefficient cannot be obtained for n-type La-doped samples.
Figure S6
Temperature ($T$) dependence of electrical resistivity ($\rho$) and Seebeck coefficient ($S$) of La-doped EuIn$_2$As$_6$ synthesized with excess amount of Eu or La. Nominal composition of starting materials is denoted in the inset.