Synthesis and thermoelectric properties of \( \text{Re}_3\text{As}_{6.6}\text{In}_{0.4} \) with \( \text{Ir}_3\text{Ge}_7 \) crystal structure

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Abstract

The \( \text{Re}_3\text{As}_{7-x}\text{In}_x \) solid solution was prepared for \( x \leq 0.5 \) by heating the elements in stoichiometric ratios in evacuated silica tubes at 1073 K. It crystallizes with the \( \text{Ir}_3\text{Ge}_7 \) crystal structure, space group \( \text{Im}^{-3}\text{m} \), with a unit-cell parameter \( a \) ranging from 8.716 to 8.747 Å. The crystal structure and properties were investigated for a composition with \( x = 0.4 \). It is shown that indium substitutes arsenic exclusively at one crystallographic site, such that the As–As dumbbells with \( d_{\text{As–As}} = 2.54 \) Å remain intact. \( \text{Re}_3\text{As}_{6.6}\text{In}_{0.4} \) behaves as a bad metal or heavily doped semiconductor, with electrons being the dominant charge carriers. It possesses high values of Seebeck coefficient and low thermal conductivity, but relatively low electrical conductivity, which leads to rather low values of the thermoelectric figure of merit.

Introduction

Thermoelectric materials with good efficiency are highly awaited by modern power engineering. Utilizing either the Seebeck or Peltier effects, it is possible to produce electricity from waste heat (e.g., that stemming from combustion in car engines) or to cool an environment under an external power supply. However, the efficiency of these processes depends on the efficiency of the thermoelectric material in question, which is defined by the value of the figure of merit \( ZT = TS^2\sigma / \kappa \), where \( T \) is the absolute temperature, \( S \) the Seebeck coefficient, \( \sigma \) the electrical conductivity, and \( \kappa \) the thermal conductivity. It is shown in the literature [1] that the best thermoelectric materials are to be sought among narrow-gap semiconductors.

Keywords:

band-structure calculations; energy conversion; \( \text{Ir}_3\text{Ge}_7 \) type; solid solution; thermoelectric material
composed of heavy elements, in which structural features favor low thermal conductivity [2]. Attempts to improve the ZT value have led to the investigation of various types of thermoelectrics beyond the long-known lead and bismuth tellurides [3,4]. Among new candidates are the filled skutterudites [5,6], semiconducting clathrates [7], disordered materials such as Zn₃Sb [8], and various inorganic and intermetallic compounds with complex crystal structures [9,10]. Compounds with the Ir₃Ge₇ structure type, namely Mo₃Sb₅,4Te₂,8 [11], Nb₅Sb₇Te₅ [12] and Re₂As₇,5Ge₅ [13], belong to the latter type of potential thermoelectric materials and have recently shown promising ZT values.

All members of the Ir₃Ge₇ family crystallize in the cubic space group I₄̅m−3m and feature the M−M dumbbells inside the Archimedean antiprism of the non-transition-element atoms. The strong hybridization of the transition-metal d-orbitals with the p-orbitals of a non-transition element may lead to the opening of a band gap near the Fermi level [14]. As a result, compounds with 55 valence electrons per formula unit (f.u.) exhibit semiconductor-like behavior. The number of valence electrons can be tuned through the solid-solution formation. For instance, Mo₂Sb₅Te₂ and Re₂As₅Ge adopt 55 e⁻ per f.u. and should be semiconductors according to the band structure calculations. Their doped analogues, Mo₃Sb₅,₄Te₁,₆ and Re₃As₆,₄Ge₀,₆, display minor deviation from 55 e⁻ per formula. They behave as heavily doped semiconductors and possess the ZT values of 0.8 at 1050 K and 0.3 at 700 K, respectively [13]. To expand the Ir₃Ge₇ family and search for new promising thermoelectrics, we investigated different ways of obtaining new solid solutions based on Re₂As₇ or Mo₃Sb₅ compounds. In this paper, we report on the synthesis of the Re₂As₇−ₓInₓ solid solution (x ≤ 0.5), its crystal and electronic structures, and its thermoelectric properties.

### Experimental

#### Synthesis and analysis

Rhenium (–325 mesh, 99.99%, Alfa Aesar) and arsenic (–70 mesh, 99.99%, Alfa Aesar) powders and indium ingots (99.95%, Sigma Aldrich) were used as received. Phase purity of the starting materials was checked by using the standard X-ray diffraction technique, and in all cases no impurity phases were found. To synthesize the title solid solution, stoichiometric quantities of the starting elements were heated in evacuated silica tubes at 1073 K for 7 days with further cooling to room temperature in a shut off furnace. Firstly, the samples were analyzed by means of X-ray powder diffraction using a Stoe STADI-IP diffractometer with Cu Kα₁ radiation (Ge monochromator, λ = 1.540598 Å). To evaluate the lattice constants of the Re₂As₇−₁In₁ solid solution, all X-ray diffraction patterns were recorded with Ge as an internal standard (a = 5.6576 Å). The data were treated with the program package Stoe WinXPOW. Secondly, the obtained samples were analyzed with a JSM JEOL scanning electron microscope operated at 20 kV and equipped with an EDX detection system INCA x-Sight. Both point-spectra acquisition and element mapping were used to investigate the elemental and phase composition of the samples.

#### Structure determination

The crystal structure was determined by the Rietveld method from the X-ray powder diffraction data. For the sample with the nominal composition Re₂As₆,₅In₀,₁, hereafter sample S₁, the data were recorded with the Bruker D8 Advance diffractometer, Cu Kα₁ radiation (Ge monochromator, λ = 1.540598 Å). For the Rietveld refinements we used the TOPAS software (version 4.2, Bruker-AXS). The refinement enabled us to determine minor quantities of three impurity phases (Table 1) that were taken into account during the subsequent refinement. The atomic parameters taken from the crystal structure of Re₂As₇ [15] were refined composition

| formula weight (g·mol⁻¹) | Re₃As₆,₇₀₀₁In₀,₃₀₀(3) |
|--------------------------|------------------------|
| T (K)                    | 1095.041               |
| wavelength (Å)           | 300                    |
| space group              | 1.540598               |
| cell dimensions, a (Å)   | Im−3m (No. 229)        |
| V (Å³)                   | 8.74231(6)             |
| calculated density (g·cm⁻³) | 668.157(14)           |
| no. of formula units per cell | 4                    |
| cell dimensions, α (°)   | 10.88                  |
| 2θ range (°)             | 17.00−85.01            |
| R_p, R_ref, GOF          | 0.056, 0.077, 1.4      |
| impurity phases (weight %) | Re 2.0%, InAs 2.3%, In₃O₃ 1.0% |
used as the starting model. The refinement showed that the unique position of the rhenium atom was fully occupied. One of the two positions of the arsenic atoms, namely, the 12d site, showed a remarkably low atomic displacement parameter and was subsequently refined as jointly occupied by indium and arsenic. The refinement led to the composition $\text{Re}_3\text{As}_{7.7(3)}\text{In}_{0.30(3)}$ in reasonable agreement with the starting (synthetic) composition. Crystallographic details of the refinement are shown in Table 1, and the atomic parameters are shown in Table 2. Selected interatomic distances are listed in Table 3.

### Table 2: Atomic coordinates and displacement parameters for S1.

| site | Wyck. | $x$     | $y$     | $z$     | $B_{iso}$ ($\text{A}^2$) | occupancy |
|------|-------|---------|---------|---------|--------------------------|-----------|
| Re   | 12e   | 0.3396(2)| 0       | 0       | 0.60(3)                  | 1Re       |
| E1   | 12d   | 1/4     | 0       | 1/2     | 0.82(11)                 | 0.90(1)As + 0.10(1)In |
| As2  | 16f   | 0.1662(2)| 0.1662(2) | 0.1662(2) | 0.82(5)                  | 1As       |

### Table 3: Selected interatomic distances for S1.

| bond | distance ($\text{Å}$) |
|------|-----------------------|
| Re–E1 $\times$ 4      | 2.597(1)             |
| Re–As2 $\times$ 4      | 2.553(1)             |
| Re–Re $\times$ 1       | 2.805(3)             |
| As2–As2 $\times$ 1     | 2.539(5)             |
| As2–As2 $\times$ 3     | 2.905(3)             |

### Electronic-structure calculations

The FPLO (full potential local orbitals) code was utilized for the electronic-structure calculations [16]. FPLO performs density functional calculations with the local density approximation (LDA) for the exchange–correlation potential [17]. The crystallographic data presented in Table 4 were used for the calculations [15]. The integrations in the $k$ space were performed by an improved tetrahedron method [18] on a grid of $16 \times 16 \times 16$ $k$ points evenly spread in the first Brillouin zone.

### Physical property measurements

For thermal transport measurements, the sample S1 was thoroughly ground and pressed at room temperature into a rectangular pellet of dimensions $8 \times 3 \times 2 \text{ mm}^3$. The density of S1 was estimated from the linear sizes of the pellet to be about 70% of the theoretical density. This pellet was used to measure the electrical conductivity ($\sigma$), the Seebeck coefficient ($S$), and the thermal conductivity ($\kappa$) in the temperature range of 77–300 K in a home-built setup. Resistance was determined from the voltage drops by applying a four-probe method in accordance with Ohm’s law, i.e., $R = \Delta V/I$. The current ($I$) was scanned in the range between 2.5 $\mu$A and 16 mA, and subsequently $\sigma$ was calculated after measuring the length between the contacts ($L$) according to $\sigma = L/(\Delta AR)$, with the area $A = 3 \times 2 \text{ mm}^2$. The Seebeck coefficient and thermal conductivity were measured by using an internal standard to determine the temperature difference in a custom-designed sample puck that was plugged into the cold finger of a closed-cycle refrigerator. All measurements were performed under dynamic vacuum.

For the magnetization measurements, powder samples of $\text{Re}_3\text{As}_7$ and S1 were loaded into plastic capsules. Measurements were performed with the VSM setup of Quantum Design PPMS in external fields of 0.1, 0.5, 1, 2, and 5 T. To estimate the diamagnetic contribution from the sample holder, an empty capsule was measured under the same conditions.

### Results and Discussion

#### Synthesis, sample characterization and crystal structure

The synthesis of the $\text{Re}_3\text{As}_7$–$x$,$\text{In}_x$ series with $x = 0, 0.2, 0.4, 0.6, 0.8$, and 1 from pure elements resulted in black powders that were stable in air. The obtained samples were analyzed by X-ray powder diffraction. All samples showed reflections of the main phase of the $\text{Re}_3\text{As}_7$ type (space group $\text{Im}–\text{3m}$), together with minor reflections of Re, InAs, and In$_2$O$_3$ admixtures, the presence of which was also confirmed with EPMA (Figure 1). In order to obtain single-phase samples, we tried to improve the synthetic procedure, but neither increasing the annealing time nor pressing the reactants into pellets led to phase-pure samples. Some general trends should be noted. For the samples with $0 \leq x \leq 0.4$, absolute intensities and, thus, quantities of admixtures remain constant, while for $x > 0.5$, quantities of Re and
InAs start to increase. Additionally, we found by a linear inter-
polation that the unit cell parameter of the Re$_3$As$_{7-x}$In$_x$ solid
solution increases up to $x = 0.5$, and then remains constant at
higher $x$ (Figure 2). All these facts suggest that the solid solu-
tion in question exists only for $x \leq 0.5$. The outermost compos-
tion Re$_3$As$_6.5$In$_0.5$ possesses exactly 55 valence electrons per
formula unit. As mentioned above, this electron concentration
should yield the semiconducting behavior for compounds with
the Ir$_3$Ge$_7$ structure type. Thus, the indium substitution for
arsenic in Re$_3$As$_7$ could be used as a chemical modification to
control transport properties of this system.

The crystal structure of the solid solution was studied for the S1
sample by the Rietveld method from X-ray powder diffraction
data (Figure 1, Table 1 and Table 2). The title compound crys-
tallizes with the Ir$_3$Ge$_7$ crystal structure (Figure 3). This struc-
ture can be described as being composed of rhenium-centered square antiprisms of E atoms, \( \text{ReE}_8 \) (E = As/In). Two square antiprisms are linked by sharing a square face. These pairs form the so-called \( \text{Re}_2\text{E}_{12} \) barrels, the main building blocks of the crystal structure. The barrels, oriented along the main crystallographic directions, form two interpenetrating 3D networks in accordance with the body-centering and, thus, build up the entire crystal structure.

The formation of the solid solution may be associated with a chemical substitution on different crystallographic sites. There are two sites forming the coordination polyhedra of E atoms in the \( \text{Ir}_3\text{Ge}_7 \) structure type (Figure 4), and the substitution is possible for both sites depending on the chemical nature of the E elements. It is known from the literature that in the case of the Ge for As substitution in the parent compound \( \text{Re}_2\text{As}_7 \), all Ge atoms enter the As2 (16f) site [13]. In contrast, we have found that when indium substitutes for arsenic in \( \text{Re}_2\text{As}_7 \), all indium atoms are on the E1 (12d) site. The preference for the certain As position depends on different aspects, including size, nuclear charge, and number of valence electrons of the heteroatom. In particular, there is an E–E single bond between atoms occupying the 16f site, with a bond distance of 2.538(5) Å. Clearly, indium does not favor such a short bond to arsenic and, therefore, avoids the occupation of this site.

In \( \text{Re}_2\text{As}_7 \), the calculated density of states at \( E = E_F \) is 8.3 states/(eV·f.u.). For the solid solution \( \text{Re}_2\text{As}_{6.7}\text{In}_{0.3} \) (the composition obtained from the Rietveld refinement of the X-ray powder diffraction data, see Table 1), the DOS is reduced to 5.15 states/(eV·f.u.), given the rigid-band shift with the assumption that \( \text{Re}_2\text{As}_7 \) possesses 56 valence electrons per f.u. and \( \text{Re}_2\text{As}_{6.7}\text{In}_{0.3} \) 55.4 electrons. Therefore, both compounds should be metallic with a Pauli paramagnetic contribution to the total susceptibility \( \chi = \chi_{\text{dia}} + \chi_P \), where \( \chi_{\text{dia}} \) is core diamagnetism, and \( \chi_P = \mu_B^2\mathcal{N}(E_F) \), with \( \mu_B \) being the Bohr magneton [20]. The formula yields \( \chi_P = 9 \times 10^{-5} \) and \( 5.5 \times 10^{-5} \) emu/mol for \( \text{Re}_2\text{As}_7 \) and S1, respectively.

Experimentally, both \( \text{Re}_2\text{As}_7 \) and S1 show substantial diamagnetism in the examined temperature range. However, the susceptibility curves, Figure 6, lie above the level of core diamagnetism \( \chi_{\text{dia}} = -3.37 \times 10^{-4} \) emu/mol, computed for a combination of \( \text{Re}^{7+} \) and As(V) [21]. Therefore, both pure and In-doped \( \text{Re}_2\text{As}_7 \) feature an additional paramagnetic contribution to the susceptibility. The experimental value of \( \chi_P = \chi - \chi_{\text{dia}} = 1.20(7) \times 10^{-4} \) emu/mol for \( \text{Re}_2\text{As}_7 \) is reasonably close to the one expected from the DOS at \( E_F \). However, the calculation of \( \chi_P \) substantially depends on the estimation method of \( \chi_{\text{dia}} \), especially for a compound that cannot be considered as ionic. For this reason, the calculated value of \( \chi_P \) may differ from the experimental one. The susceptibility of the S1 slightly decreases upon cooling but starts increasing below 80 K. While the low-temperature upturn could be due to a small number of paramagnetic impurities, the conspicuous increase in \( \chi \) above 80 K does not conform to the Pauli paramagnetism and reflects deviations of S1 from a simple metal.

Electronic structure, magnetic and thermo-electric properties

The computed density of states for \( \text{Re}_2\text{As}_7 \) is shown in Figure 5. The Fermi level lies slightly above the gap of 0.8 eV that separates the conduction band from the valence band. The nonzero DOS at \( E_F \) implies metallic behavior for the undoped \( \text{Re}_2\text{As}_7 \). Additionally, the steep slope of the DOS curve near \( E_F \) should lead to a high Seebeck coefficient according to \( S \sim \frac{1}{N\mathcal{N}(E_F)} \mathcal{N}(E) / \mathcal{N}(E_F) [19], \) provided that the system is made semiconducting by doping. Indeed, the absolute values of \( S \) for \( \text{Re}_2\text{As}_{6.4}\text{Ge}_{0.6} \) exceed 150 \( \mu \)V K\(^{-1} \) at high temperatures, thus leading to high values of \( ZT \) [13].
Figure 7 compiles the plots of the electric conductivity ($\sigma$), Seebeck coefficient ($S$), thermal conductivity ($\kappa$), and $ZT$ in the temperature range of 77–300 K for S1. $S$ is negative in this temperature range, evidencing that the S1 is an n-type conductor. However, the $\sigma$-versus-$T$ behavior for the S1 sample is neither metallic nor classically semiconducting, because $\sigma$ increases almost linearly with temperature. Thus, S1 can be regarded as a bad metal or degenerate semiconductor, considering the possible presence of defects, such as vacancies in its crystal structure, which was proposed earlier for Re$_3$As$_7$ [15]. In the Ir$_2$Ge$_7$ family, Re$_3$As$_{7-x}$Ge$_x$ exhibits n-type conductivity [13], while Mo$_3$Sb$_{5.5}$Te$_{2.5}$ is a p-type conductor [11]. The obtained values of $S$ for S1 are comparable with those for Re$_3$As$_{6.4}$Ge$_{0.6}$ and Mo$_3$Sb$_{5.4}$Te$_{1.6}$: $-49$, $-72$, and $+55 \mu$V·K$^{-1}$ at 300 K, respectively [11,13]. Moreover, the extent of the substitution x in the Re$_3$As$_{7-x}$In$_x$ solid solution can be further optimized, and possibly lead to larger values of $S$. Unfortunately, the S1 displays considerably lower values of the electrical conductivity compared to both Re$_3$As$_{7-x}$Ge$_x$ and Re$_3$As$_{7-x}$Sn$_x$ (0.1 $\leq$ x $\leq$ 0.6) [22]. For instance, the room-temperature value of 1090 $\Omega$·cm$^{-1}$ for Re$_3$As$_{6.4}$Ge$_{0.6}$ [13] is about 3000 times larger than the observed value of 3.8 $\Omega$·cm$^{-1}$ for S1.

The thermal conductivity of the sample S1 is quite low. Its room-temperature value is 0.3 W·m$^{-1}$·K$^{-1}$, which is an order of magnitude lower than for the Ge- and Sn-substituted compounds. This may be caused by two factors: Firstly, it could be attributed to the preference of indium atoms for only one position within the crystal structure (increased structural complexity); secondly, relatively low density of the sample (about 70%) may diminish the thermal conductivity due to the sample porosity. The total thermal conductivity is a sum of the electronic ($\kappa_e$) and lattice ($\kappa_L$) parts. Taking into account the rather low electrical conductivity and applying the
Wiedemann–Franz relation $\kappa_e = \sigma L T$, where $L$ is the ideal Lorentz number, we estimate that the electronic part of the total thermal conductivity is negligibly small, and the observed value is essentially the lattice contribution to the thermal conductivity.

Combining the electrical conductivity, Seebeck coefficient and thermal conductivity, we calculate the temperature dependence of $ZT$ shown in Figure 7. $ZT$ increases with temperature, and reaches $ZT = 0.0008$ at room temperature, which is 30 times lower than for Re$_3$As$_7$-Ge$_x$ [13]. Given the compositional width of the Re$_3$As$_7$-In$_x$ solid solution and the low thermal conductivity of the investigated sample, we note that the optimum combination of $S$ and $\sigma$ for Re$_3$As$_7$-In$_x$ is still to be found.

Conclusion

Chemical modification of Re$_3$As$_7$ resulted in the formation of the new Re$_3$As$_7$-based solid solution Re$_3$As$_7$-In$_x$ ($x \leq 0.5$) with an Ir$_2$Ge$_7$ type of crystal structure. The indium for arsenic substitution occurs exclusively on the 12d site, thus keeping intact the As–As dumbbells with $d_{\text{As–As}} = 2.538(5)$ Å. While Re$_3$As$_7$ shows a Pauli paramagnetic contribution to the magnetic susceptibility in line with the results of band-structure calculations, the $S$ sample behaves as a bad metal or heavily doped semiconductor, with electrons being the dominant charge carriers. This compound combines low thermal conductivity with a relatively low electrical conductivity, and therefore, its thermoelectric figure of merit $ZT$ reaches only 0.0008 at room temperature. Further optimization of the thermoelectric properties by varying the chemical composition of Re$_3$As$_7$-In$_x$ is proposed.

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