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Complete List of Authors:	BOURGÈS, Cédric; National Institute for Materials Science, International Center for Young Scientist (ICYS) Zhang, Wenhao; National Institute for Materials Science, WPI-MANA; University of Tsukuba Graduate School of Pure and Applied Sciences Raut, Krushna Kumari; National Institute for Materials Science, WPI-MANA; University of Tsukuba Graduate School of Pure and Applied Sciences Owada, Yuka; National Institute for Materials Science, Electron Microscopy Analysis Station/High-Resolution Group Kawamoto, Naoyuki; National Institute for Materials Science, Electron Microscopy Analysis Station/High-Resolution Group Mitome, Masanori; National Institute for Materials Science, Electron Microscopy Analysis Station/High-Resolution Group Kobayashi, Kazuaki; National Institute for Materials Science, WPI-MANA Halet, Jean-Francois; National Institute for Materials Science, CNRS-Saint Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK) Berthebaud, David; National Institute for Materials Science, CNRS-Saint Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK); Institut des Matériaux de Nantes Jean Rouxel, Nantes Université, CNRS Mori, Takao; National Institute for Materials Science, WPI-MANA; University of Tsukuba Graduate School of Pure and Applied Sciences

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Investigation of Mn Single and Co-doping in Thermoelectric CoSb₃-Skutterudite: A Way Toward a Beneficial Composite Effect

Cédric Bourgès^{1*}, Wenhao Zhang^{2,3}, Krushna Kumari Raut^{2,3}, Yuka Owada⁴, Naoyuki Kawamoto⁴, Masanori Mitome⁴, Kazuaki Kobayashi², Jean-François Halet⁵, David Berthebaud^{5,6}, and Takao Mori^{2,3*}

¹ International Center for Young Scientists (ICYS), National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

²WPI-MANA, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

³Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8577, Japan

⁴ Electron Microscopy Analysis Station/High-Resolution Group, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044 Japan

⁵ CNRS-Saint Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

⁶Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France

Corresponding Authors: BOURGES.Cedric@nims.go.jp, MORI.Takao@nims.go.jp

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ABSTRACT:

We report here the first in-depth theoretical and experimental investigations of Mn substitution within the CoSb₃-skutterudite. A systematic and comprehensive approach was employed to first determine the feasibility of single/co-substitution for Mn with Te and then assess its effect. Subsequently, experimental realization of the samples was conducted. We were able to highlight a low solubility limit of Mn as a single dopant and provide evidence that the substitution stabilizes *p*-type conduction as predicted *via* DFT calculations. Then, we reveal the prevalent formation of the composite MnTe/CoSb₃-skutterudite phases instead of the expected favorable co-substitution. This unexpected composite formation induces a beneficial effect, maximizing the Seebeck coefficient and leading to a record power factor $PF \approx 4.7 \text{ mW/m.K}^2$ at 725 K for an unfilled skutterudite compound. ($PF = S^2\sigma$ with *S*, Seebeck coefficient; σ , electrical conductivity)

1 INTRODUCTION

Thermoelectric (TE) power generation represents a valuable solution for supplying a substantial amount of IoT applications and contributing to a sustainable future.^{1,2} By utilizing appropriate devices, TE modules can effectively harvest waste heat from the surrounding environment and convert it into valuable electrical power. The TE conversion efficiency is quantified by the dimensionless figure of merit $zT = PF T \kappa^{-1} = S^2 \sigma T \kappa^{-1}$ (PF , power factor; T , absolute temperature; S , Seebeck coefficient; σ , electrical conductivity; κ , thermal conductivity). In the range of ambient to mid-temperature (300 – 800 K), several compounds were reported with zT values above unity and beyond, such as Bi_2Te_3 ,^{3,4} PbTe ,^{5,6} GeTe ,^{7,8} as well as the Mg_3Sb_2 -based compounds^{9,10} which have been extensively studied recently, leading to a theoretical conversion efficiency of 7 – 14%. However, most of those materials contain expensive and/or toxic elements which limit or even prevent their large applications. Other families of compounds, such as the oxide and sulfide compounds also appear to be attractive due to their low cost and/or eco-friendlier compositions but still show relatively modest zT values.¹¹ Among these families, there are ZnO ,^{12,13} some natural sulfide-based minerals such as the recent colusites $\text{Cu}_{26}\text{T}_2\text{M}_6\text{S}_{32}$ ($T = \text{V, Nb, Ta, Cr, Mo, W, Ti, M} = \text{Ge, Sn, Sb}$)^{14,15} to mention a few.

In this context, the skutterudite CoSb_3 and derivatives represent an attractive solution for achieving the best trade-off between performance and scalability. Within the state-of-the-art thermoelectrics, CoSb_3 has been at the center of extensive investigations as a suitable compound where the concept of phonon-glass-electron crystal (PGEC) can apply for effectively decoupling its thermal and electrical transport properties and promoting a high figure of merit ($zT > 1$).¹⁶ Indeed, it has been extensively studied during the past two decades and it is one of the few TE materials which step up to the stage of real applications such as for the next generation of RTG (Radioisotope Thermoelectric Generator) in the National Aeronautics and Space Administration (NASA) to replace the actual $\text{PbTe/GeTe-AgSbTe}_2$ (TAGS) couple, for instance.^{17,18} Multiple intrinsic advantages of the skutterudites include strong mechanical strength,¹⁹ reasonable thermal stability,²⁰ and both conductivity p - and n -types are achieved with high thermoelectric performances.

Additionally, the skutterudite-type structure is famous for its two icosahedral voids ($2a$ site: $(0;0;0)$), present in its body-centered cubic structure (space group $Im\bar{3}$; $a \approx 9.04 \text{ \AA}$), which can be ‘filled’ by additional elements.^{21,22} In general, the filler elements occupying the cavities in the structure are weakly bonded with their surrounding Sb atoms, allowing a rather efficient phonon scattering *via* rattling motion. Interestingly, this scattering does not significantly affect the electronic transport properties of the skutterudites, leading to impressive performances with zT values largely exceeding the unity in the

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3 medium temperature range and even reaching a record value above 2 in the case of multi-filler-containing
4 compounds assisted with strain defects.²³ However, the most efficient fillers are lanthanides, actinides,
5 alkaline or alkaline-earth metals, raising some issues regarding the cost and availability of rare-earth
6 elements, as well as the chemical stability and oxidation sensitivity of such filled-skutterudites.
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11 In the present study, we focus on the investigation of inserting Mn element as a single and co-
12 dopant within the CoSb₃-skutterudite structure. Prior studies presented a possibility of Mn insertion^{24–26}
13 in CoSb₃. The purpose of this study was to evaluate the effect of a strategic magnetic element on the
14 thermoelectric properties of *n*-type skutterudites. Magnetism has been noted to effectively enhance the
15 Seebeck coefficient in various recent examples such as via spin-carrier interaction,^{27–31} spin fluctuation,
16 or spin entropy.^{32,33} The induced magnetic moment here can potentially influence the carriers through
17 spin-carrier interactions affecting and enhancing the Seebeck coefficient.²⁹ Besides, co-doping is an
18 attractive strategy that can be used to effectively enhance the solubility limit of substituted elements,
19 defects, or impurities enabling the adjustment of the physicochemical, electronic, and magnetic properties
20 of materials.³⁴ The well-known Te substitution was selected as co-dopant to i) stabilize the *n*-type
21 conduction with high initial electronic transport properties, and ii) reduce the thermal conductivity of the
22 unfilled skutterudite.^{35–43} Theoretical investigations were conducted to assess the feasibility of single/co-
23 doping and predict their influence on the electronic transport properties of CoSb₃. Then, an experimental
24 investigation of the Mn-doped CoSb₃ and Mn-Te-codoped CoSb₃ was performed by solid-liquid state
25 synthesis method followed by spark plasma sintering (SPS). A structural and microstructural analysis was
26 systematically performed and discussed together with the characterization of the transport properties.
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41 2 EXPERIMENTAL PROCEDURES

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44 **Sample Preparation.** Samples of Mn_{*x*}Co_{1-*x*}Sb₃ (*x* = 0, 0.05, 0.10) and Mn_{*x*}Co_{1-*x*}Sb_{2.85}Te_{0.15} (*x* = 0.005,
45 0.02, 0.04, 0.06, 0.08, 0.10) were prepared by melt-quenching processing. This was followed by extensive
46 annealing in evacuated sealed tube processing and final consolidation by spark plasma sintering (SPS).
47 Firstly, the stoichiometric ratio of high-purity shot elements (5 N) was weighted and sealed in carbon-
48 coated evacuated quartz tubes. The tubes were heated up to 1423 K (heating rate of 100 K/h) and quenched
49 in water. The resulting ingots were sealed in a new evacuated quartz tube and followed by an annealing
50 at 873 K (heating rate of 100 K/h) for 100h to improve the homogeneity of the sample and facilitate the
51 reaction of the residual free Sb. The annealed pellets were ground and sieved down to < 212 μm before
52 being sintered (SPS-1080 – SPS Syntex Inc.) at 873 K for 5 min. (heating rate ~100 K/h) with an axial
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3 pressure of ~50 MPa in a 10 mm diameter graphite die and partial vacuum atmosphere. The sintered
4 pellets were then polished and cut to the required shapes and dimensions for the property measurements.
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8 **Characterizations.** The crystal structure of different samples was investigated by X-ray diffraction
9 (XRD) technique in the θ - 2θ mode within a 10° - 100° range (Smart Lab3 Rigaku Corporation apparatus).
10 X-ray powder diffraction patterns were refined by Rietveld analysis using the FullProf and WinPLOTR
11 software packages.^{44,45} The shape of the diffraction peaks was modeled using a Thompson-Cox-Hastings
12 pseudo-Voigt profile function. Zero-point shift, asymmetry parameters, and lattice parameters were
13 systematically refined, and the background contribution was manually estimated.
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19 Observations of fractured cross-sections of densified pellets by scanning electron microscopy
20 (SEM) were performed using a Hitachi SU-8000 microscope and the chemical component analysis was
21 carried out by energy dispersive spectroscopy (EDS) on polished surfaces.
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25 The carrier concentration and mobility were obtained from Hall Effect measurements in AC
26 transport by using a PPMS (Quantum design) from -5 to +5 T.
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29 The electrical conductivity (σ) and Seebeck coefficient (S) were simultaneously measured by the
30 four-probe method from 300 K up to 725 K using a ZEM-3 (ULVAC Advance-Riko) device under partial
31 helium pressure. The estimated measurement uncertainties were fixed at 8% for the electrical conductivity
32 and 6% for the Seebeck coefficient.⁴⁶
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37 The temperature-dependent thermal diffusivity (D) was measured using the laser flash diffusivity
38 method with an LFA-467 Hyperflash (Netzsch) instrument on graphite-coated disc-shaped samples of 10
39 mm diameter and ~2 mm thickness. The temperature-dependent heat capacity (C_p) was derived using a
40 standard sample (pyroceram-9060) with LFA-467, which was in good agreement with the expected
41 Dulong-Petit C_p value. The total thermal conductivity was calculated using the formula, $\kappa = D \times C_p \times \rho$,
42 where ρ is the density of the sample (measured using Archimedes' principle). In some cases, to better
43 understand the thermal transport properties, the contributions from electronic and lattice parts in the total
44 thermal conductivity were separated. The lattice thermal conductivity (κ_{att}) was estimated from κ by
45 subtracting the electronic contribution (κ_e) via the Wiedemann-Franz law, using the following equation,
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$$\kappa_e = L\sigma T \quad (1)$$

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56 where κ_e is the electronic thermal conductivity, and $L = 2.44 \times 10^{-8} \text{ V}^2/\text{K}^2$ is the Lorenz number. The
57 uncertainty in the results was estimated to be 11% and 10% for the values of electrical and thermal
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transport properties, respectively, and that for the overall zT was 15%.⁴⁶ Error bars are not shown in the figures in order to improve their readability.

Zero-field-cooled (ZFC), field-cooled-cooling (FCC), and field-cooled-warming (FCW) magnetization measurements were carried out on powder samples (~ 20 - 40 mg) from 2 to 300 K using a Magnetic Properties Measurement System (MPMS, Quantum Design) apparatus.

Theoretical Calculations. Density Functional Theory (DFT) calculations were carried out for the ground state of CoSb₃ and its doped derivatives. Self-consistent calculations were performed using a plane wave expansion basis set as implemented in the *Quantum Espresso* package⁴⁷ with the generalized gradient approximation pseudopotential (PBE-GGA) formulated with the projector augmented-wave (PAW) method.⁴⁸⁻⁵⁰ A kinetic energy cutoff of 150 Ry and a 7 times higher charge density cutoff were used.

Defect formation energy calculations were performed to identify the defect sites of Mn/Te and their corresponding charge states. Mn and Te defects were relaxed at the Γ point of the Brillouin zone (BZ) while the total energy was calculated using a $4 \times 4 \times 4$ k -grid. Spin-nonpolarized calculations were used to obtain defect formation energies while collinear spin-polarized calculations were used for the band structure. In CoSb₃, defects can be positioned in one of the four different positions: 1) atomic substitution, 2) void-center, 3) 7-fold, and 4) 6-fold (the notation used is the same as that used in previous works).⁵¹⁻⁵³ In the latter three cases the extrinsic atoms form interstitial defects. The defect formation energy was given by the following equation,^{54,55}

$$E_{def}(q) = E_{supercell}^{def}(q) - \sum_{\alpha} N_{\alpha} \mu_{\alpha} + q\mu_e + E_{corr}$$

where $E_{def}(q)$ is the defect formation energy of a charged defect, q refers to the charge state of the defect, $E_{supercell}^{def}(q)$ is the total energy of the charged defect-containing supercell, N is the number of atoms in the defect supercell and μ their corresponding chemical potential, μ_e is the chemical potential of the electron, and E_{corr} is the correction energy due to the mirror charges in the DFT calculations.⁵⁴⁻⁵⁶ The chemical potentials of the atoms were determined under the equilibrium condition of phase coexistence. For Te doping, we calculated the chemical potential considering the phase equilibrium between CoSb₃, CoSb₂, and Sb₂Te₃. For Mn substitution, we chose the equilibrium CoSb₃, CoSb₂, and MnSb while for interstitial doping we chose the equilibrium between CoSb₃, Sb, and MnSb. Equaling the atomic chemical potential in the equilibrium phase gives the chemical potential used in the above equation.

3 RESULTS AND DISCUSSION

Effect of Mn Doping on Band Structure. Before carrying out any experiments, we decided to perform DFT calculations to study the effect of Mn doping and Mn/Te co-doping in CoSb_3 . First, the defect positions of the Te and Mn dopants were determined from the calculated defect formation energy of different possible defect sites as a function of the electronic chemical potential and defect charge states, as shown in **Figure 1**. For both cases, substitution defects are energetically favored near the conduction band minimum (CBM) for Te doping and valence band maximum (VBM) for Mn doping. Indeed, the formation energy of the different dopant sites agrees systematically with that obtained in previous calculations.^{51–53} In the *n*-type region, Te substitution has a defect charge state of +1 with respect to Sb, while the Mn substitution has a defect charge state of -2 with respect to Co.⁵⁶

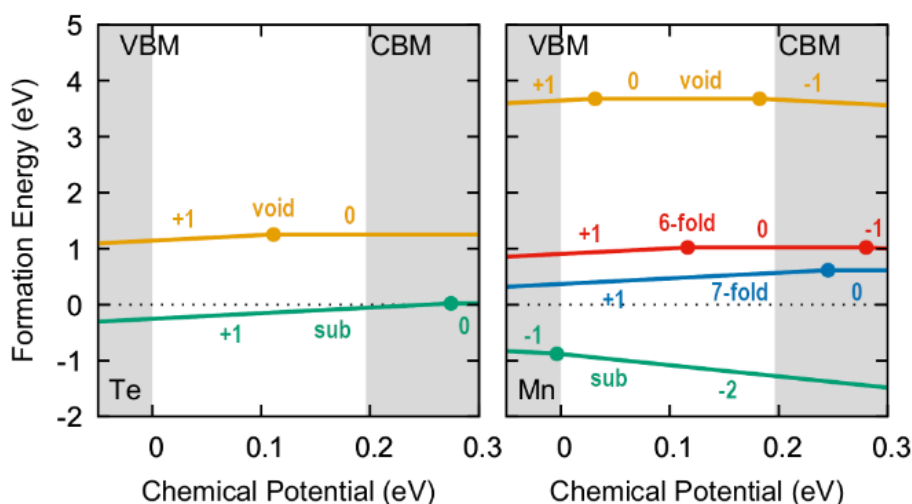


Figure 1 Calculated defect formation energy for Te (left) and Mn (right) defects in CoSb_3 . The green, orange, blue, and red colors refer to defects positioned at the four different possible positions, i.e., substitution, void-center, 7-fold, and 6-fold sites. The corresponding stoichiometries were $\text{Co}_{32}\text{Sb}_{95}\text{Te}$ (sub), $\text{Co}_{32}\text{Sb}_{96}\text{Te}$ (void), $\text{MnCo}_{31}\text{Sb}_{96}$ (sub), and $\text{MnCo}_{32}\text{Sb}_{96}$ (void, 6-fold and 7-fold).

The effect of Mn substitution and co-doping on the electronic band structure of CoSb_3 is shown in **Figure 2**. The shape of the band structure and the band gap of 0.2 eV of the pure skutterudite CoSb_3 is in good agreement with previous theoretical calculations.^{38,52,57,58} The top of the valence band around Γ consists mainly of Sb *p* states, showing an almost linear Kane band dispersion, while the bottom of the conduction band is mainly of Co 3*d* character. The introduction of Mn substitution leads to (flat and spin-polarized) impurity bands near the top of the valence band (**Figure 2b**) and a magnetic moment of 1.97 μ_B per substitutional defect, corresponding in turn to the difference in the number of valence electrons between Mn and Co. Except for the appearance of flat impurity bands around the Fermi level (orange

dotted line), the valence band dispersion remains essentially the same as that of pure CoSb_3 , indicating that the effect of Mn substitution is localized.

For the co-doped systems, we considered that the main effect of co-doping with Te was to introduce additional electrons to the system (rigid band model approach). Therefore, **Figure 2c and d** shows the corresponding band structures of the Mn-substituted CoSb_3 with an additional number of electrons corresponding to co-doped systems. It turns out that these additional electrons fill the empty impurity bands deriving from Mn-inserted atoms reducing correspondingly their magnetic moments. When all the impurity bands are filled, the local magnetic moments on the defect sites vanish and the filled impurity bands sit just below the Fermi level. This indicates that by controlling the ratio between Mn and Te co-doping, some magnetism can be introduced in the CoSb_3 system, and precisely tuned. Indeed, this result provides the opportunity to investigate a potential correlation between magnetism and thermoelectric properties. Furthermore, a change in the band structures for both *p*-type and *n*-type transport properties is noticeable, suggesting a possible improvement of the thermoelectric properties of these systems.

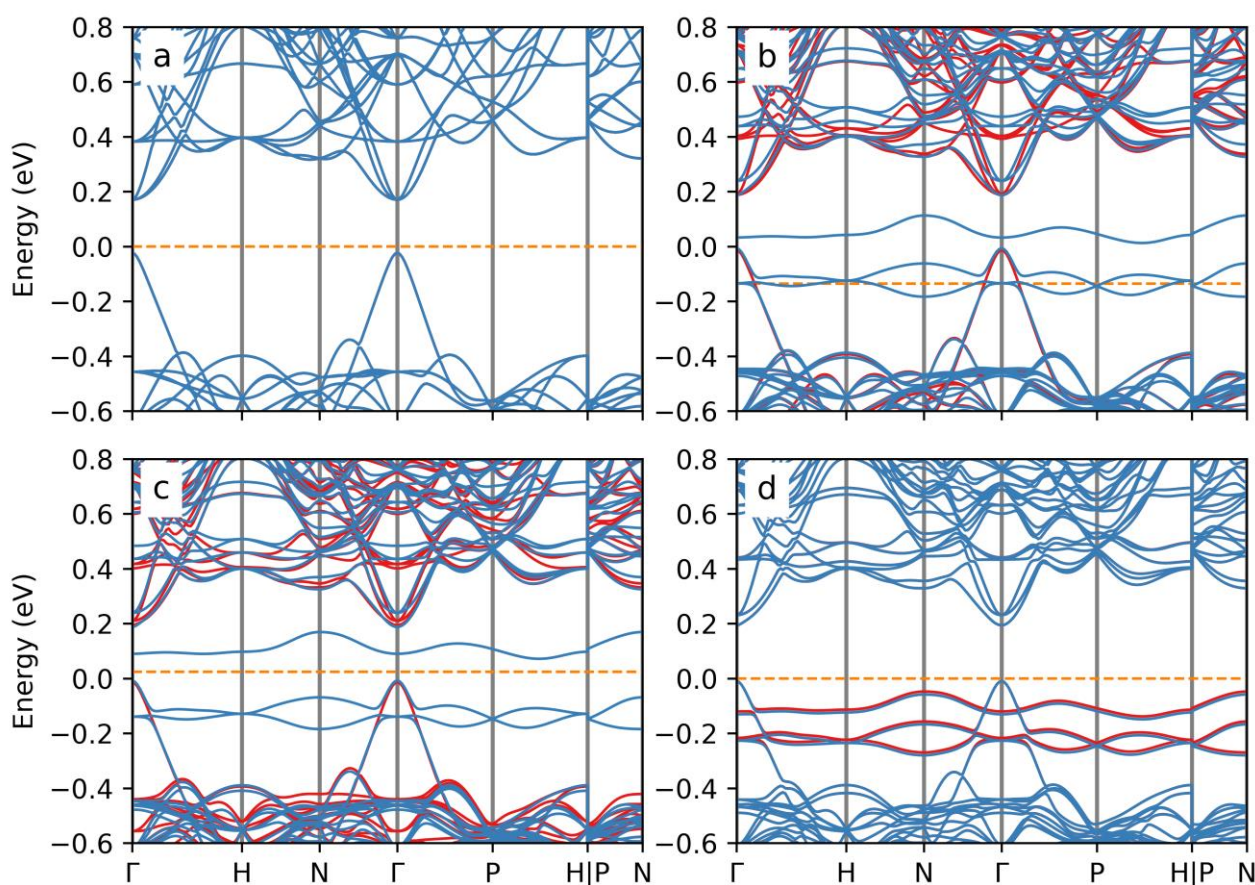


Figure 2 Electronic band structure of a) CoSb_3 , b) $\text{Mn}_{0.03}\text{Co}_{0.97}\text{Sb}_3$ ($\text{MnCo}_{31}\text{Sb}_{96}$ (sub)), c) $[\text{Mn}_{0.03}\text{Co}_{0.97}\text{Sb}_3]^-$ corresponding to formally $\text{Mn}_{0.03}\text{Co}_{0.97}\text{Sb}_{2.97}\text{Te}_{0.03}$, and d) $[\text{Mn}_{0.03}\text{Co}_{0.97}\text{Sb}_3]^{2-}$ corresponding formally to $\text{Mn}_{0.03}\text{Co}_{0.97}\text{Sb}_{2.94}\text{Te}_{0.06}$. Spin-up and spin-down bands are plotted in blue and red, respectively. The orange dotted line indicates the Fermi level.

Mn Single-doped Influence in the TE Properties of CoSb_3 . Figure 3 shows the X-ray powder diffraction (XRPD) patterns of the final Mn-doped samples densified by SPS. In all patterns, the main diffraction peaks corresponding to the CoSb_3 -skutterudite structure ($Im\bar{3}$, $a \approx 9.04$ Å) can be observed with a trace amount of free Sb up to $x = 0.05$. Above this content, reflections barely observable at $2\theta = 29.2^\circ$, 40.1° , and 43.4° agree with the formation of a tiny amount of the MnSb phase ($P6_3/mmc$, $a \approx 4.17$ Å; $c \approx 5.76$ Å) which attests to an apparent solubility limit of the Mn within the CoSb_3 crystal structure. The formation of MnSb was confirmed through a Rietveld refinement analysis (Figure S1) as well as by SEM observations (Figure S2). The lattice parameter follows a pseudo linear trend up to $x = 0.05$ in relation with the Mn content increase within the CoSb_3 which is sustained by an EDX analysis (Table S1). However, beyond $x > 0.05$ the solubility limit is reached and the lattice parameter does not vary further as the favorable formation of MnSb occurs. The solubility limit is consistent with the valence electron count (VEC) deficiency in the Mn-doped CoSb_3 structure, as explained below. In the case of the prototypical MX_3 skutterudites ($M = \text{Co}, \text{Rh}, \text{and Ir}$) a VEC of 24 per formula is generally observed.⁵⁹ Assuming a successful tiny substitution of Co by Mn – thermodynamically stable according to the DFT calculations (see above) – the 2-electron poorer Mn element will reduce the theoretical VEC down to 23.8 for the $x = 0.1$ (see Table 1) explaining the p -type conduction observed even for a very small Mn amount. This result is similar to that of the Cr-doped CoSb_3 which highlighted a low solubility value of the $3d$ elements in the main structure.⁶⁰

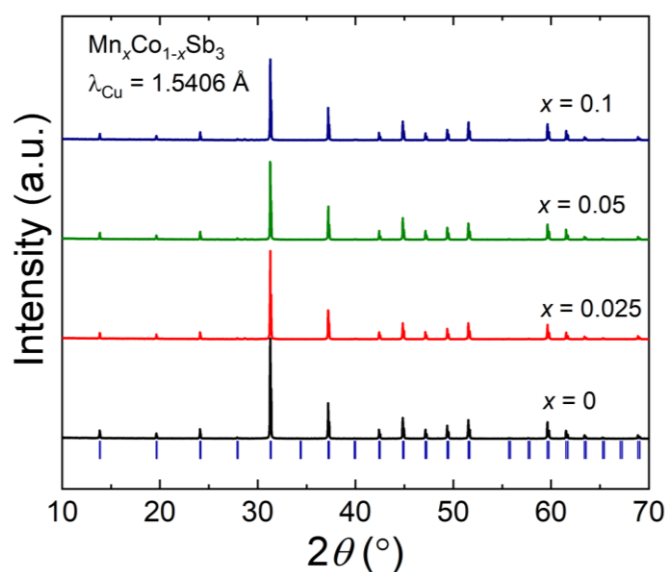


Figure 3 X-ray powder diffraction pattern of the $\text{Mn}_x\text{Co}_{1-x}\text{Sb}_3$ SPS samples ($x = 0, 0.025, 0.05, \text{ and } 0.1$).

Table 1 Rietveld refinement parameter of the X-ray powder diffraction patterns of the $Mn_xCo_{1-x}Sb_3$ SPS samples and theoretical valence electron count (VEC) per formula.

$Mn_xCo_{1-x}Sb_3, I m\bar{3}, \lambda_{Cu}$						
x	a (Å)	V (Å ³)	χ^2	R_{Bragg}	R_F	VEC
0	9.0345	737.42	1.65	5.21	5.24	24
0.025	9.0337	737.21	1.74	6.28	6.48	23.95
0.05	9.0336	737.18	1.88	8.32	6.81	23.9
0.1	9.0336	737.19	1.98	8.96	8.05	23.8

x	B_{iso} (Co)	Co (occ.)	B_{iso} (Sb)	y (Sb)	z (Sb)	Sb (occ.)
0	0.5	1	0.5	0.33438	0.15823	1
0.025	0.5	1	0.5	0.33395	0.15798	1
0.05	0.5	1	0.5	0.33406	0.15797	1
0.1	0.5	1	0.5	0.33367	0.15712	1

The Seebeck coefficient S and the electrical resistivity ρ of the Mn-doped $CoSb_3$ samples over the temperature are sketched and compared to a pristine $CoSb_3$ reference sample in **Figure 4**. It is noteworthy to remind that in pure $CoSb_3$ the carrier type obtained at room temperature depends on whether the samples are synthesized under Sb-rich or Sb-deficient conditions. Samples grown under Sb-rich conditions will be p -type since this corresponds to the formation of holes in the valence band promoted by the absence of some Co atoms. On the contrary, samples synthesized with Sb-deficient conditions will lead to an excess of electrons in the conduction band and consequently n -type behavior. No excess Sb was used in our synthesis, but our reference sample shows n -type conduction at room temperature which turns to p -type conduction above 330 K as expected from a slightly Sb deficient sample. Indeed, Mn doping changes the n -type character into a stable p -type conduction all over the temperature range (**Figure 4a**). This constitutes the first report illustrating that Mn substitution can modify the thermoelectric properties in skutterudites. The Seebeck coefficient $|S|$ increases gradually from $x = 0.025$ to 0.05 in the single-phase region before decreasing together with the formation of $MnSb$ for $x = 0.1$ implying that the secondary phase affects the electrical transport properties. This increase in the Mn-doped sample is attributed to the formation of the flat impurity bands near the top of the valence band, which enhances the density of states around the Fermi level (see **Figure 2b** above). Indeed, this increase of DOS must play a significant role in the enhancement of the Seebeck coefficient which according to the Mott's formula for a metal/degenerate-semiconductor can be defined as:⁶¹

$$S = \frac{\pi^2 k_B^2 T}{3 e} \left(\frac{d\{\ln[\sigma(E)]\}}{dE} \right)_{E=E_F}$$

with k_B , the Boltzmann's constant and e the electron elementary charge. The large magnitude of the Seebeck coefficient at room temperature is also consistent with a low carrier concentration in the range of $10^{16} - 10^{17} \text{ cm}^{-3}$ as confirmed by Hall effect measurements. The S and σ vs. the hole concentration p plots (**Figure 5a**) reveal a parabolic and linear trend confirming the carrier concentration's dependence on the electrical transport properties despite the apparent lack of trend with the nominal Mn-content. Irrespective of the Mn content, the electronic transport properties in the near room temperature range (300 – 450 K) are significantly enhanced with an averaged three-time improvement ($PF_{\text{av}300-450 \text{ K}}$) (**Figure 4c**). This improvement can certainly be attributed to the large p -type Seebeck coefficient and the reduced electrical resistivity. However, in the higher temperature range ($T > 450 \text{ K}$) PF_{max} of the undoped sample remains the highest one due to a slightly larger electrical conductivity. It is likely related to the increased carrier scattering at higher temperatures due to the impurity phases (Sb and Sb/MnSb) occurring only in Mn-doped samples. Indeed, those trends follow well the calculated weighted mobilities showing larger values in the low temperature for the Mn-doped samples which converge in the high temperature ranges $T > 450 \text{ K}$ to similar values (**Figure 5b**). The weighted mobility can be defined as:⁶²

$$\mu_W = \frac{3h^3}{8\pi e\rho(2m_e k_B T)^{3/2}} \left[\frac{\exp\left[\left(\frac{|S|}{k_B/e}\right) - 2\right]}{1 + \exp\left[-5\left(\frac{|S|}{k_B/e}\right) - 1\right]} + \frac{\frac{3}{\pi^2} \frac{|S|}{k_B/e}}{1 + \exp\left[5\left(\frac{|S|}{k_B/e}\right) - 1\right]} \right]$$

with μ_W the weighted mobility, ρ the electrical resistivity, T the absolute temperature, S the Seebeck coefficient, and $\frac{k_B}{e} = 83.3 \mu\text{V}/\text{K}$. The large weighted mobilities show an increasing dependence in temperature for samples with $x > 0$, suggesting that the defects (Mn ionized dopants) are responsible for the superior PF . However, at the temperature $T > 450 \text{ K}$, the decreasing dependence confirms that the usual phonon scattering mechanism is at work for the electrical transport properties and limits the role of the impurities.

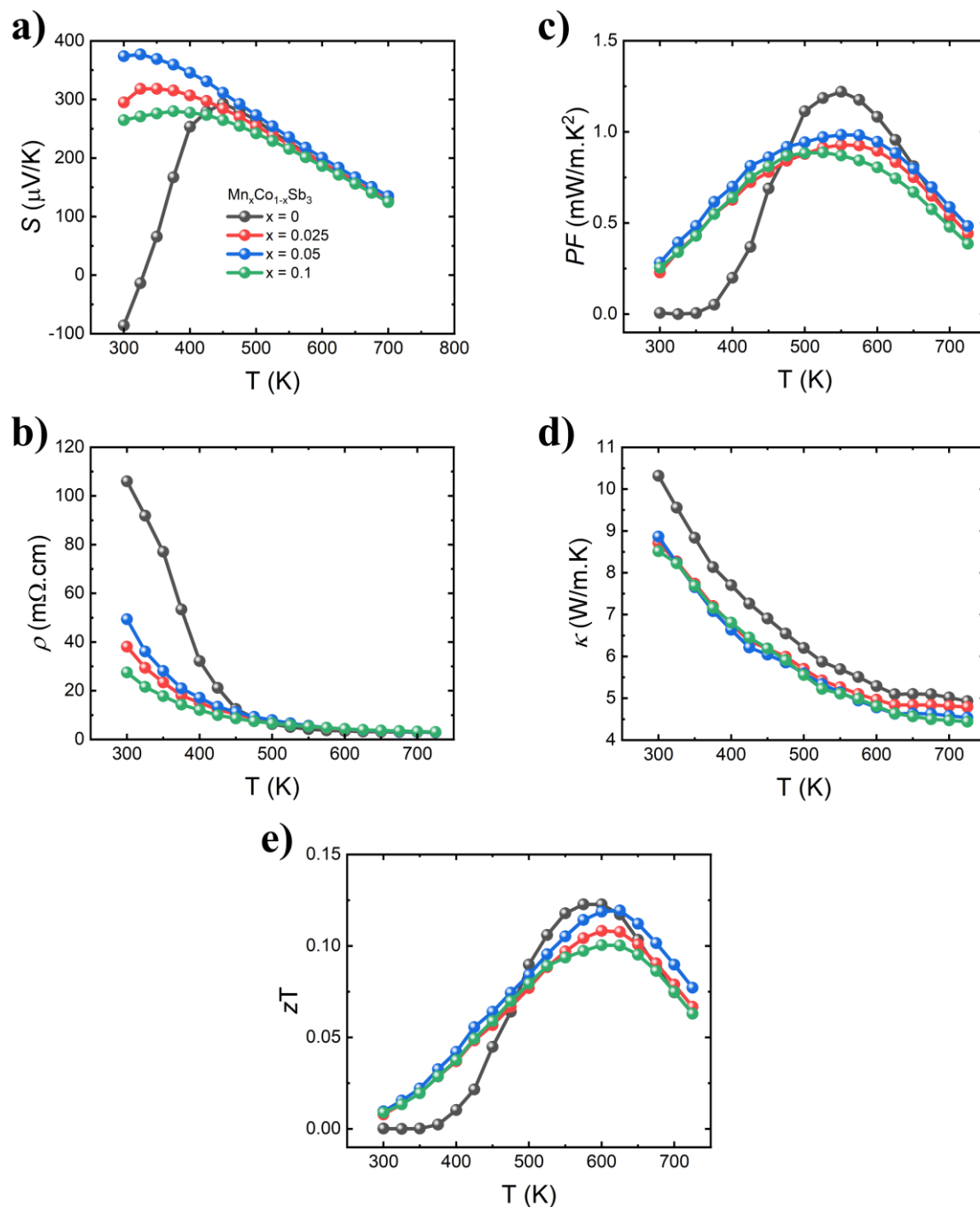


Figure 4 a) Seebeck coefficient S , b) electrical resistivity σ , c) power factor PF , d) thermal conductivity κ , and e) figure of merit zT as function of temperature of $Mn_xCo_{1-x}Sb_3$ SPS samples. The estimated measurement uncertainties are 6% for the S , 8% for ρ , 11% for the PF , 10%, for the κ and 15% for the zT .⁴⁶

The thermal conductivity of the Mn-doped samples diminishes slightly with respect to that of pure $CoSb_3$ throughout the entire temperature range (Figure 4d). This diminution is in an agreement with the slight mass fluctuation scattering of the phonons induced by the substitution of Co (58.933 g/mol) by Mn (54.938 g/mol). It is not excluded that the presence of $MnSb$ impurity within the matrix for $x = 0.1$ might

contribute to this decrease but its role is considered as minor due to the small amount in presence. Anyway, the thermal conductivity remains still too large for promoting a better figure of merit and the zT values follow in turn the trend of the PF variations (**Figure 4e**).

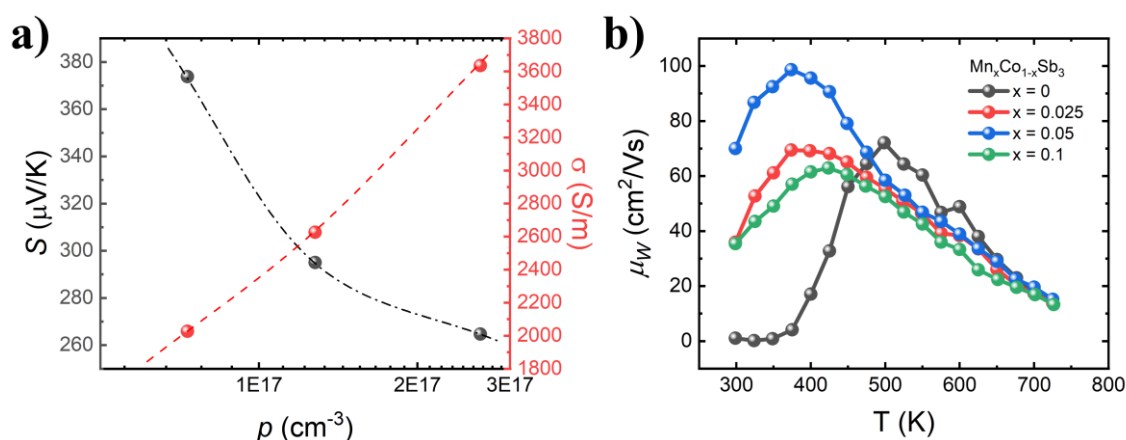


Figure 5 a) S and σ dependence upon hole concentration p at 300 K, and b) weighted mobility dependence in temperature of $Mn_xCo_{1-x}Sb_3$ SPS samples.

Mn Co-doped Influence in the TE Properties of n -type $CoSb_3$. We further used Te co-doping to investigate the n -type transport region of the $CoSb_3$ skutterudite with Mn impurities. The approach was to over-dope with Te to compensate the Mn doping effect demonstrated above. Indeed, the Te-single doping on the $CoSb_3$ matrix has been extensively explored theoretically and experimentally within the past two decades.^{35–43} The role of Te as an electron donor as well as a phonon scattering center due to the mass fluctuation effect have been demonstrated and used for promoting large figures of merit in unfilled $CoSb_3$ -skutterudites. From the electronic band-structure point of view, although Te doping only slightly influences the shape of the top of the valence band, it somewhat shifts the Fermi energy level up to the conduction band and reduces the width of the bottom of the conduction band. This variation of the band gap and conduction band width implies some increase in both carrier concentration and effective mass for an overall enhanced electrical performance. Experimentally, Te-doping in $CoSb_{3-y}Te_y$ was investigated in the formula range $0 \leq y \leq 0.20$, the latter constituting the solubility limit of Te content within the bulk $CoSb_3$ structure. Classically, the optimum figure of merit zT is obtained with the content $y \approx 0.125$ due to the trade-off between the reduction of the thermal conductivity and the maintaining of a large PF independently of the process employed.^{37,40,43} To achieve higher zT and compensate the theoretical electron deficiency induced by Mn substitution, the Te content for the co-doping was fixed at a slightly over doping $y = 0.15$.

Figure 6 shows the X-ray powder diffraction (XRPD) patterns of the final $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$ densified samples. In all patterns, the main diffraction peaks corresponding to the $CoSb_3$ -skutterudite structure ($Im\bar{3}$, $a \approx 9.04$ Å) can be observed. In the case of the Mn-based doped samples ($x > 0$), Mn

doping promotes the formation of the MnTe phase ($P 6_3/m m c$, $a \approx 4.14 \text{ \AA}$; $c \approx 6.70 \text{ \AA}$)⁶³ confirmed through an EPMA mapping analysis (**Figure 7**) and its corresponding point analysis (**Figures S3-S4**).

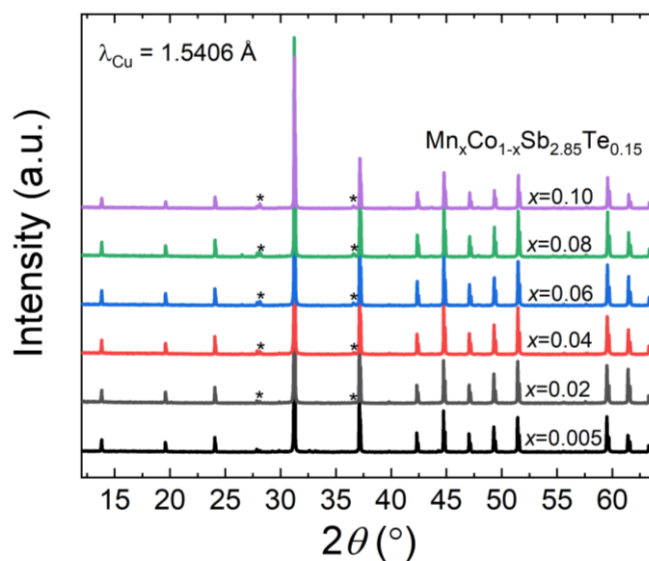


Figure 6 X-ray powder diffraction patterns of the $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$ SPS samples after annealing.

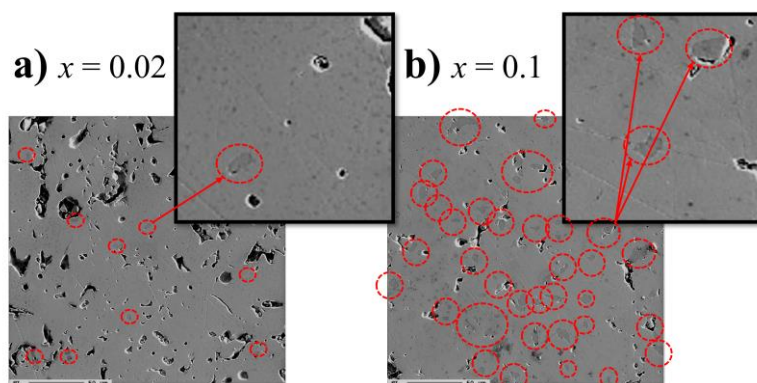


Figure 7 EPMA images of the $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$ SPS samples ($x = 0.02$ (a) and 0.1 (b)) after annealing. The red circles indicate the MnTe inclusions within the $CoSb_3$ matrix.

Contrary to the Mn single-doped samples, Mn substitution in the Co site appeared not to be favorable in presence of Te and led to the unavoidable precipitation of nano-microscale size MnTe particles. The distribution of the MnTe inclusions is homogeneous with a varying size distribution ranging from the nanometer scale to few microns, characterized by an angular medium sphericity roundness. A Rietveld refinement allowed us to estimate the wt.% of MnTe in each sample. The results are shown in **Table 2**. The MnTe-phase content increases with x content from 1.15 wt.% for $x = 0.02$ to 4.76 wt.% for $x = 0.1$, as illustrated with the EPMA images shown in the **Figure 7**.

Table 2 Rietveld refinement parameters of the X-ray powder diffraction patterns of the $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$ SPS samples and estimation of the mass fraction percentage (wt.%) of each phase (CoSb₃ and MnTe)

$Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$, $Im\bar{3}$, λ_{Cu}							
x	a (Å)	V (Å ³)	χ^2	R_{Bragg}	R_F	wt.% (CoSb ₃)	wt.% (MnTe)
0.005	9.050(1)	741.1	2.27	9.99	6.7	100	-
0.02	9.049(1)	741.0	2.61	8.86	7.6	98.9	1.1
0.04	9.046(1)	740.1	2.61	8.26	6.44	98.1	1.9
0.06	9.043(1)	739.4	2.65	8.81	7.62	96.8	3.2
0.08	9.040(1)	738.9	2.91	10.2	7.34	96.0	4.0
0.1	9.039(1)	738.7	2.79	12.7	10.3	95.8	4.2

x	B_{iso} (Co)	Co (occ.)	B_{iso} (Sb/Te)	y (Sb/Te)	z (Sb/Te)	Sb (occ.)	Te (occ.)
0.005	0.292	1	0.246	0.3339	0.1581	0.95	0.05
0.02	0.292	1	0.246	0.3337	0.1583	0.95	0.05
0.04	0.292	1	0.246	0.3341	0.1580	0.95	0.05
0.06	0.292	1	0.246	0.3342	0.1578	0.95	0.05
0.08	0.292	1	0.246	0.3336	0.1580	0.95	0.05
0.1	0.292	1	0.246	0.3339	0.1576	0.95	0.05

High accuracy of the EPMA point analysis revealed only some trace of Mn in the main CoSb₃ matrix confirming that the presence of Te prevents the substitution of the Co site due to the low enthalpy of formation of MnTe, reported to be $\Delta H_{298}^S = -40.2 \text{ kJ.g.at}^{-1}$.⁶⁴ In order to confirm the presence/absence of Mn within the Te-doped CoSb₃ structure, a STEM investigation was performed in two characteristic zone axes (namely [110] and [001]), (see **Figure 8a** and **8b**, respectively) in order to observe accurately the icosahedral voids (2a site: (0; 0; 0)) together with the global structural arrangement. As a result, the icosahedral voids appeared free of any filler and no intensity defects are observable in the HAADF image (**Figure 8a**). A TEM-EDS mapping (**Figure 8b**) confirmed that the Te substitution occurs at the Sb site but could not confirm the presence of Mn within the structure. To the best of our knowledge, the community has always been divided regarding the possibility or not that the tellurium element fills the skutterudite voids rather than substitutes the Sb site. It is noteworthy to point out here that the current STEM-HAADF we performed constitutes the first evidence that Te does not fill the icosahedral void of the skutterudite structure. Indeed, from a chemical point of view, it is hard to believe that Te anions can fill anionic Sb voids.

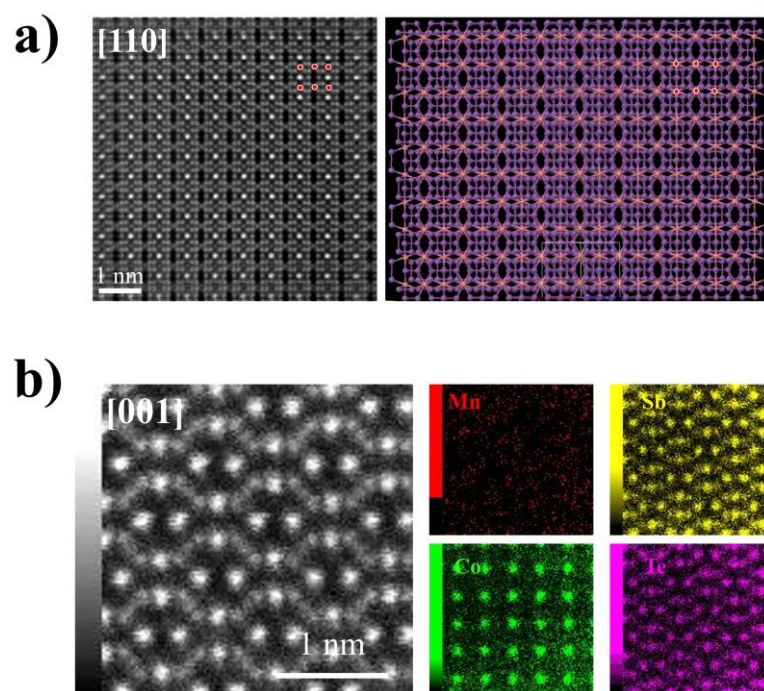


Figure 8 STEM-HAADF images of a) the [110] axis and the corresponding structural model, and b) the [001] axis and the corresponding EDS mapping of the $Mn_{0.1}Co_{0.99}Sb_{2.85}Te_{0.15}$ SPS sample.

The TE properties of the Mn/Te-co-doped $CoSb_3$ samples are illustrated in **Figure 9**. All samples exhibit a *n*-type conduction consistently with the Te-doping effect as reported in several previous studies (**Figure 9a**) and expected due to the Te electron donor properties.^{35–43} Interestingly, the Mn *x* content induces a large increase of the absolute values of the Seebeck coefficient $|S|$ in the whole temperature range. Despite the concurrently rise of the electrical resistivity (**Figure 9b**), PF increases massively in the room temperature range from 2.29 to 3.56 mW/m.K² at 300 K for $x = 0.005$ and 0.1, respectively. This kind of large increase is usually not observed for unfilled $CoSb_3$ skutterudites. Interestingly, such a large enhancement of the electrical transport properties of the Mn-containing samples at room temperature is supported by the calculated weighted mobilities (**Figure 10b**) (see the Mn single doped section above). It can be observed that the weighted mobilities are overall large and decrease with temperature, a characteristic of most of the good thermoelectric materials, confirming that the electron-phonon scattering mechanism is dominant.⁶² We can notice that the weighted mobilities range in the values $\mu_w > 300$ cm²/V at 300 K and reach the impressive value of 397 cm²/V at 300 K for $x = 0.1$, comparable indeed to that reported for PbTe.⁶⁵

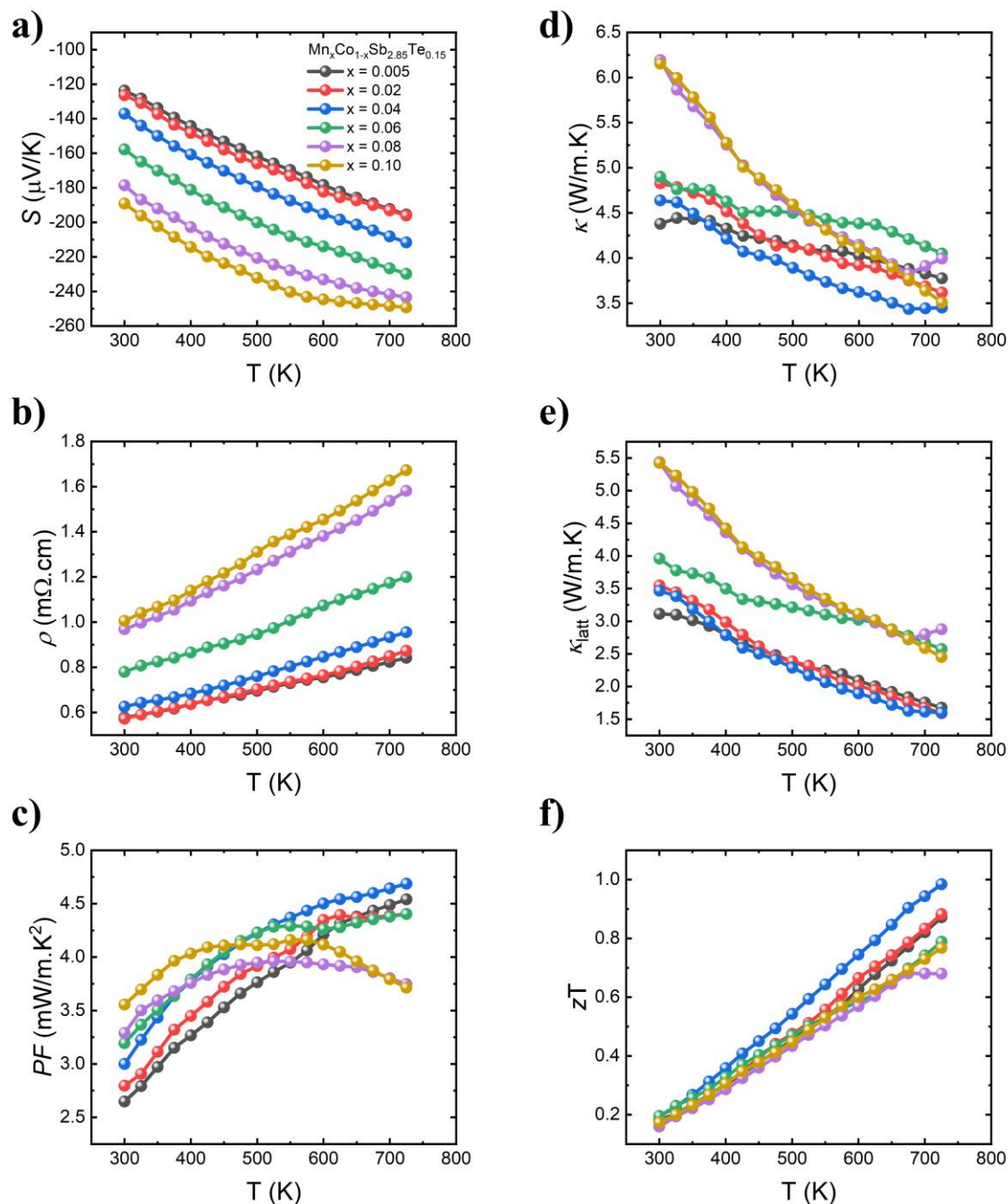


Figure 9 a) Seebeck coefficient S , b) electrical resistivity σ , c) power factor PF , d) total thermal conductivity κ , e) lattice part of the thermal conductivity κ_{latt} , and f) figure of merit zT as function of temperature of the $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$ SPS samples. The estimated measurement uncertainties are 6% for the S , 8% for ρ , 11% for the PF , 10%, for the κ and 15% for the zT .⁴⁶

The initial contribution to the increase of the Seebeck coefficient can be attributed to the decrease of the carrier concentration n resulting from a higher (total) Mn content, as demonstrated in **Figure 9**. Upon formation of the MnTe phase, the electron donor effect caused by the Te content in $CoSb_3$ is reduced (Figures S4-S5) since Te preferentially reacts with Mn. Consequently, the electron concentration

decreases, as indicated by the Hall effect measurements, from $n = 4.05 \times 10^{20}$ to $1.20 \times 10^{20} \text{ cm}^{-3}$ at 300 K, respectively, for $x = 0.02$, and 0.1 (**Figure 10a**). However, the slight carrier concentration variation cannot explain solely the major increase of the Seebeck coefficient, as evidenced by comparing the $\text{Mn}_x\text{Co}_{1-x}\text{Sb}_{2.85}\text{Te}_{0.15}$ samples with the single Te-doped series with the ratio $0.15-x$ (**Figure S5**). Indeed, the presence of the MnTe phase introduces a composite effect that may bring two additional contributions: i) the larger band gap of MnTe ($E_g \approx 0.6 - 1.2 \text{ eV}$) compared to that of CoSb_3 ($E_g \approx 0.2 \text{ eV}$) could be favorable to an energy filtering effect in the case of an energy level alignment between the electronic structures of CoSb_3 and MnTe around the Fermi level,^{66,67} and/or ii) the (known) antiferromagnetic state of the MnTe phase can bring some local magnetic moments which can *couple* with the carriers of doped- CoSb_3 at the interface between the CoSb_3 matrix and the MnTe precipitate.^{68,69} In both cases, the carriers should acquire a heavier effective mass leading to a superior Seebeck coefficient. To elucidate point ii), the magnetic behavior of the series ($x > 0.005$) was probed to get an insight regarding the Mn doping (**Figure S6**). All the susceptibilities were normalized with respect to the CoSb_3 molar mass rather than that of the Mn content to conduct a comparative analysis. The apparent magnetic susceptibility increases with the Mn content in the near-room temperature range sustaining a possible role of magnetism in the observed properties upon co-doping. However, the presence of the antiferromagnetic (AFM) MnTe phase within the matrix ($T_c = 308 \text{ K}$, $\mu_{\text{eff}} \approx 5 \mu_B$ per unit cell, $\theta \approx -600 \text{ K}$) renders the determination of the residual magnetic moment within CoSb_3 somewhat hazardous.^{63,70}

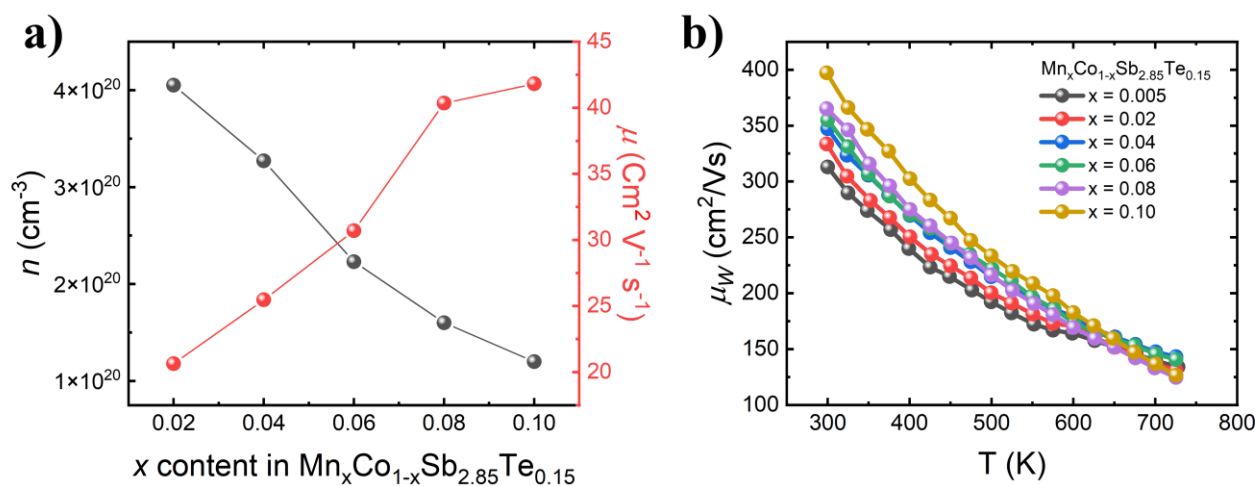


Figure 10 a) Carrier concentration n and mobility μ at 300 K, and b) weighted mobility dependence in temperature of the $\text{Mn}_x\text{Co}_{1-x}\text{Sb}_{2.85}\text{Te}_{0.15}$ SPS samples

Together with PF , the thermal conductivity κ increased with the increasing Mn content (**Figure 9d**). This increase is in large part attributed to the lattice contribution κ_{latt} (**Figure 9e**), attesting a change

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3 in the phonon transport mechanism. This reveals that thermal transport is sensitive to the MnTe formation.
4 Two set of samples can be separated: *i*) from $x = 0.005$ to 0.04 , and *ii*) from $x = 0.06$ to 0.1 . For *i*), the
5 formation of MnTe is estimated to be below 2 wt.% (**Table 2**) and therefore the amount of the MnTe
6 dispersion in CoSb_3 remains small, as illustrated in the EPMA image for $x = 0.02$ (**Figure 7a**).
7 Interestingly, κ_{latt} remains at its lowest values despite the expected reduction in Te content within the
8 CoSb_3 matrix. This indicates a proficient effect of the precipitate to act as a scattering center, enabling a
9 slight reduction of κ (**Figure 9d**). At higher Mn content, κ increases gradually near room temperature,
10 approaching a value close to that of the undoped CoSb_3 . This increase is directly related to a massive rise
11 of κ_{latt} of more than 50% in the whole temperature range for the samples $x = 0.08$ – 0.1 . This is consistent
12 with the large formation of MnTe, which reduces the Te content within the co-doped CoSb_3 structure and
13 subdues its effect on the reduction of the thermal transport. As a result, the figure of merit is improved for
14 $x = 0.04$ to maximum values of $zT \approx 1$ at 725 K thanks to a slight reduction of κ and a significant
15 enhancement of PF . It is noteworthy that this ultra-high value of $PF = 4.7 \text{ mW/m.K}^2$ at 725 K has been
16 rarely obtained for rare-earth free skutterudites.
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29 4 CONCLUSIONS

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31 In summary, we have reported here the first theoretical and experimental investigation of the Mn
32 doping effect on CoSb_3 -skutterudite. An original approach was adopted focusing first on single Mn-doped
33 $\text{Mn}_x\text{Co}_{1-x}\text{Sb}_3$ samples before exploring co-doping with Te to prepare $\text{Mn}_x\text{Co}_{1-x}\text{Sb}_{2.85}\text{Te}_{0.15}$ samples,
34 examining their effect on both conduction types. Theoretical DFT results revealed that single Mn doping
35 was feasible. This was successfully confirmed experimentally with the obtention of pure samples with a
36 low solubility of Mn ($x \leq 0.05$ in $\text{Mn}_x\text{Co}_{1-x}\text{Sb}_3$) sitting at the Co site up to a certain amount of Mn
37 substitution where a small amount of the binary MnSb phase is formed. Regarding the transport properties,
38 we show for the first time that Mn stabilizes *p*-type conduction with a large Seebeck coefficient resulting
39 from a small reduction of the valence electron count per formula due to some Co substitution. This allows
40 an improvement of the power factor as well as the resulting figure of merit zT in the near-room temperature
41 range ($T < 450 \text{ K}$). Co-doping with Te was then realized highlighting that the formation of the additional
42 MnTe phase was unexpectedly prevalent with respect to Co substitution. The structural investigation
43 evidenced for the first time that Te is substituting Sb and does not fill the icosahedral voids present in the
44 CoSb_3 skutterudite. We also revealed that a significant enhancement of the power factor can be achieved
45 with ultra-high value of 4.7 mW/m.K at 725 K seldomly reported for rare-earth free skutterudites due to
46 a spectacular increasing of the Seebeck coefficient in the co-doped CoSb_3 skutterudite. Combined
47 experimental and theoretical findings indicate that a plethora of factors beneficially participate to the large
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3 enhancement of the Seebeck coefficient, successfully allowing to achieve a maximum zT value of 1 at
4 725 K. Such a high value can in turn be controlled by the formation of some MnTe secondary phase which
5 slightly helps to reduce the thermal conductivity and to maximize an unexpected power factor to a value
6 which competes with that reported for the expensive rare-earth filled skutterudites. This achievement
7 contributes to build up a divergent approach to the development of a new generation of sustainable TE
8 materials by investigating the magnetic as well as the composite effect in order to provide stable, cost
9 efficient and high performance materials for thermoelectricity based on unfilled skutterudites.
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15 ASSOCIATED CONTENT

16 SI- Supporting Information

17 The Supporting Information is available free of charge at <https://pubs.acs.org/doi/XXX>

18 Refined powder X-ray diffraction pattern of the sample $Mn_xCo_{1-x}Sb_3$ for Mn = 0.1 after SPS. SEM image
19 and EDS mapping of the polished sample $Mn_xCo_{1-x}Sb_3$ for Mn = 0.1 after SPS. Extended point analysis
20 by EPMA of the $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$ SPS samples ($x = 0.02$ and 0.1). Seebeck coefficient S , as function
21 of temperature of the $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$ and corresponding compensated Te-single doped $CoSb_{3-y}Te_y$
22 SPSed samples. Temperature-dependent magnetic susceptibility χ and $1/\chi$ of the $Mn_xCo_{1-x}Sb_{2.85}Te_{0.15}$
23 SPSed. Energy Dispersive X-ray analysis of $Mn_xCo_{1-x}Sb_3$.(PDF)
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33 AUTHOR INFORMATION

34 Corresponding Authors.

35 **Cédric Bourgès** - International Center for Young Scientists (ICYS), National Institute for Materials Science, 1-1
36 Namiki, Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0001-9056-0420, Email:
37 BOURGES.Cedric@nims.go.jp,
38
39

40
41 **Takao Mori** - WPI-MANA, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044,
42 Japan and Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba,
43 Ibaraki 305-8577, Japan; orcid.org/0000-0003-2682-1846, Email: MORI.Takao@nims.go.jp,
44
45
46
47
48

49 Authors.

50
51 **Wenhao Zhang** - WPI-MANA, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044,
52 Japan and Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba,
53 Ibaraki 305-8577, Japan, orcid.org/0000-0003-3359-1882
54
55
56
57
58
59
60

Krushna Kumari Raut - WPI-MANA, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan and Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8577, Japan, orcid.org/0009-0009-7945-2838

Yuka Owada - Electron Microscopy Analysis Station/High-Resolution Group, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Naoyuki Kawamoto - Electron Microscopy Analysis Station/High-Resolution Group, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, orcid.org/0000-0002-2022-3987

Masanori Mitome - Electron Microscopy Analysis Station/High-Resolution Group, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, orcid.org/0000-0003-1192-9838

Kazuaki Kobayashi - WPI-MANA, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan, orcid.org/0000-0002-3440-5730

Jean-François Halet - CNRS-Saint Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, orcid.org/0000-0002-2315-4200

David Berthebaud - CNRS-Saint Gobain-NIMS, IRL 3629, Laboratory for Innovative Key Materials and Structures (LINK), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan and Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France, orcid.org/0000-0002-2892-2125

Author Contributions.

Conceptualization, Methodology, Validation- CB; *Formal Analysis-* CB, WZ, YO & NK; *Investigation-* CB, WZ & KKR; *Writing-Original Draft-* CB; *Writing- Review & Editing-* CB, WZ, DB, JFH; *Resources, Funding acquisition-* TM; *Supervision-* TM, MM & KK

Notes.

The authors declare no conflict of interest.

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