Compatibility approach for the improvement of oxide thermoelectric converters for industrial heat recovery applications

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New ceramic $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9+\delta}/\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_{3-\delta}$ thermoelectric generators with different cross section areas A_p and A_n of the p- and the n-type leg are fabricated, characterized, and tested at high temperatures in long-term tests. The variation of the measured power output and the efficiency with changing A_p/A_n ratio is discussed and compared with calculations based on the measured material properties. The highest conversion efficiencies are reached for ratios close to the one predicted by the compatibility approach, whereas an improper choice of A_p/A_n leads to a strong reduction of the efficiency. A volume power density of 1.4 W/cm^3 and an efficiency of 1.08% are found for the most promising generator (temperature difference $\Delta T = 734 \text{ K}$ and $A_p/A_n = 1.12$). The results reveal the major importance of the A_p/A_n ratio for the conversion efficiency and subsequently cost and weight reduction issues, both crucial for a large scale application of thermoelectric converters. Additionally, the oxide generators proved to be very reliable, as after more than 110 h of high temperature energy conversion, no degradation is observable. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4926476>]

I. INTRODUCTION

Even modern industrial casting processes consume several GWh of electricity and release waste heat from large induction furnaces to melt tons of metals. For the implementation of thermoelectricity in such a potential high temperature energy harvesting application, the fabrication of reliable, economical, and efficient thermoelectric generators is necessary. Oxides are very promising candidates as the operation temperatures of other thermoelectric materials like bismuth telluride ($T_{\max} \leq 550 \text{ K}$),¹ skutterudites ($T_{\max} < 673 \text{ K}$),^{2,3} and half-Heusler compounds ($T_{\max} \leq 850 \text{ K}$)^{4–6} are moderately low and the materials deteriorate in oxidizing atmospheres.

In literature, various high temperature oxide converters were manufactured and characterized,^{7–13} with many of them based on the promising p-type misfit-layered $\text{Ca}_3\text{Co}_4\text{O}_9$ and its Gd or Bi substituted compounds. The cobalt oxide was combined with n-type materials like $\text{La}_{0.9}\text{Bi}_{0.1}\text{NiO}_3$,^{8,14,15} $(\text{ZnO})_7\text{In}_2\text{O}_3$,⁷ $\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}$,¹¹ and CaMnO_3 based materials with La, Nd, Mo, Sm, or Nb substitution.^{16–19} The highest measured power densities so far are 0.45 W/cm^2 or 0.96 W/cm^3 for a $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9/\text{LaNiO}_3$ generator for a hot side temperature of 1073 K .¹⁵ Besides, for a $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9/\text{La}_{0.9}\text{Bi}_{0.1}\text{NiO}_3$ module, a volume and a mass power density of 0.66 W/cm^3 and 0.14 W/g were measured.⁸ However, converter efficiencies are rarely reported and the necessary adjustment by applying the compatibility approach for the optimization of the generator

dimensions and geometries is still an open task. While for a $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9/\text{Ca}_{0.9}\text{Yb}_{0.1}\text{MnO}_3$ module, a theoretical conversion efficiency of about 3% was predicted from the material properties,²⁰ much lower measured efficiencies of 0.15%–0.082%, and 0.37% were stated for $\text{La}_{1.98}\text{Sr}_{0.02}\text{CuO}_4/\text{CaMn}_{0.98}\text{Nb}_{0.02}\text{O}_3$ ^{21,22} and $\text{Ca}_3\text{Co}_4\text{O}_9/2\%\text{Al-doped ZnO}$ converters,²³ respectively. For the latter converter, a much better efficiency of 1.16% could be achieved for additional segmentation of the p-type leg with $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{CoSb}_{0.8}\text{Sn}_{0.2}$.²³ For a single p-type segmented leg constructed from $\text{Ca}_{2.8}\text{Lu}_{0.15}\text{Ag}_{0.05}\text{Co}_4\text{O}_9$ and the half-Heusler alloy $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{CoSb}_{0.8}\text{Sn}_{0.2}$, a maximum efficiency of about 5% was measured at $T_h = 1153 \text{ K}$. Although it is the highest reported value for an oxide based leg, the experimental value reaches only 65% of the theoretical efficiency due to parasitic resistances.²⁴ A further increase of the total efficiency can also be achieved by cascading of different conventional converts with improved efficiency.

This work focuses on the enhancement of non-segmented oxide converters by changing the A_p/A_n ratio and shows that experimental converter efficiencies larger than 1% can be reached, which are comparable to state-of-the-art segmented oxide converters. Diverse high T oxide converters are manufactured, but usually no attention is put on adjusting the A_p/A_n ratio or determining the efficiency. Hence, in this work, we illustrate the importance of optimizing oxide converters according to the A_p/A_n ratio and address the determination of the efficiency using the compatibility approach introduced in the following.

As stated by Snyder *et al.*, the efficiency of a thermoelectric material depends on the reduced current density

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u that is defined as the ratio of electrical current density (J) to conductive heat flux.²⁵ For a specific reduced current density u , the efficiency reaches a maximum. This ratio is called the compatibility factor s . It can be calculated from the materials properties and depends on temperature (T). The reduced current density u^* , leading to the highest efficiency of the entire leg, has to be chosen considering $s(T)$. For the combination of p- and n-type material, it is important that both legs can work with their most efficient u^* . In this case, the legs are compatible with each other. This compatibility can be reached by adjusting the ratio A_p/A_n of the cross section areas A_p and A_n of the p- and the n-type leg. However, the most efficient A_p/A_n ratio depends on the hot side temperature T_h and the cold side temperature T_c of the legs, which can strongly fluctuate in time for, e.g., mobile applications.²⁶ Therefore, knowledge about the dependency of the efficiency on the cross section ratio A_p/A_n and its temperature dependency can help to tailor thermoelectric converters accordingly. On top of that, an adjustment allows for cost, volume, or weight reduction, making the converters more economical.

In this work, the effect of a varied cross section area ratio A_p/A_n on the efficiency of thermoelectric generators is investigated theoretically and experimentally. Therefore, a series of 4-leg thermoelectric generators with $A_p/A_n = 0.74, 1.01, 1.12, 1.24$, and 2.74 is fabricated from the p-type $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$ and the n-type $\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_{3-\delta}$. These oxides stand out due to their relatively high thermoelectric Figure of Merits (ZT), non-toxicity, and high chemical and temperature stability ($T_{\max} \approx 1200\text{ K}$)²⁷ in air. Moreover, their low material and synthesis costs^{28,29} allow the fabrication of competitive thermoelectric converters. As mechanically stable generators with low contact resistances can be fabricated using Ag-paste mixed with cobalt oxide powder soldered via hot pressing,¹⁵ this material combination provides a good basis for studying the influence of the leg geometry. For both materials, the Seebeck coefficient (α), the electrical (σ), and the thermal conductivities (κ) are measured and used to calculate the most efficient cross section ratio, the maximum power output, and the efficiency for different temperature gradients. Furthermore, a comparison of the theoretical key figures and the experimental data is made.

II. THEORETICAL MODEL

According to Snyder *et al.*,^{25,30} the conversion efficiency $\eta(T) = \eta_r \eta_C$ of a material at temperature T can be calculated from the Carnot efficiency $\eta_C = \frac{T_h - T_c}{T_h}$ and the reduced efficiency

$$\eta_r = \frac{u(\alpha - u\kappa/\sigma)}{u\alpha + 1/T} \quad (1)$$

using the average values σ , α , κ , and T of the considered interval $\Delta T = T_h - T_c$. The reduced efficiency depends on the relative current density $u = \frac{J}{\kappa \nabla T}$. It reaches a maximum value $\eta_r^{\max}$ for u equal to the compatibility factor $s = \frac{\sqrt{1+ZT}-1}{\alpha T}$, where $Z = \frac{\alpha^2 \sigma}{\kappa}$. To reach a high total leg efficiency, u should be close to s in the whole leg.

Within the leg, $u(T)$ is fixed by the solution of the one-dimensional steady-state heat equation, which can be approximated by a recursive formula.³⁰ For the recursive calculation, the starting value $u_{0,h}$ at the hot side of the leg can be chosen freely, which corresponds to choosing the external load resistance in the experimental setup. Based on the chosen $u(T)$, the total leg efficiency $\eta_{\text{leg}} = \int_{T_c}^{T_h} \eta(T) dT$ is found by integration over the leg's temperature range. Finally, the most efficient relative current $u^*(T)$, which maximizes the efficiency η_{leg} of the whole leg can be found via a variation of $u_{0,h}$. More details and model calculations can be found elsewhere.^{30–32}

In a thermoelectric converter, the same electrical current $I = J_p A_p = -J_n A_n$ flows in both legs, and thus,

$$\frac{A_p}{A_n} = \frac{-J_n}{J_p} = \frac{-\int_{T_c}^{T_h} u_n \kappa_n dT}{\int_{T_c}^{T_h} u_p \kappa_p dT}. \quad (2)$$

From this equation, the ratio $(A_p/A_n)^*$ for which both legs work with their highest efficiency can be calculated using $u_p = u_p^*$ and $u_n = u_n^*$. Additionally, for a generator with arbitrary A_p/A_n the equation fixes u_n as soon as u_p is chosen. These u determine the efficiencies η_p and η_n of the single legs, and thus, the power output $P = \eta_p Q_p^h + \eta_n Q_n^h$ and the efficiency

$$\eta_{n+p} = \frac{\eta_p Q_p^h + \eta_n Q_n^h}{Q_p^h + Q_n^h} \quad (3)$$

of the whole generator. Thereby, the heat flow

$$Q = J \Phi A \quad (4)$$

is determined by the thermoelectric potential $\Phi = \alpha T + \frac{1}{u}$ and Q_p^h and Q_n^h are the heat flows entering the hot sides of the legs. Finally, the maximum of the power output or the efficiency is found by a variation of u_p . The associated reduced current densities are u_p^{**} and u_n^{**} .

While for the compatibility approach, $u(T)$ is considered to depend only on T , a related concept developed in the 1960s³³ shows that u is also a function of the local electrochemical potential. Thus, the latter approach is more accurate, but our results show that Snyder's approximation of $u(T)$ forms a good basis for the A_p/A_n optimization.

III. MATERIALS AND EXPERIMENTAL METHODS

To synthesize 0.14 mol $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$, 0.549 mol Co metal and 0.42 mol CaCO_3 were suspended in about 300 ml water. Under cooling, 400 ml of nitric acid (>69% aq.) were added continuously. The resulting clear pink solution was transferred into about 200 ml of an aqueous solution of 1.94 mol citric acid. After drying at 573 K, the residuum of the gel was crushed and calcined in air at 1073 K for 10 h. Next, a pellet ($\varnothing = 20\text{ mm} \times h = 11\text{ mm}$) was sintered in vacuum by Spark Plasma Sintering (FCT-HP D 10, 50 MPa,

heating 100 K/min to 1123 K, then 25 K/min to 1153 K and 5 min holding time. Cooling at 25 MPa and 25 K/min to 773 K followed by free cooling). Finally, the legs for the generators and samples for the material characterizations were cut from the same pellet. The samples were postannealed in air at 1123 K for 20 h to ensure similar and homogeneous oxygen content. The highest ZT was found perpendicular to the pressing direction. Therefore, the modules were manufactured accordingly ($Q \perp$ pressing direction). The material for the n-type legs ($\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_{3-\delta}$) of the generators was synthesized via a citrate process.²⁹ A hydrostatically pressed (2000 bar) green body ($\varnothing = 40 \text{ mm} \times h = 9 \text{ mm}$) was produced and pre-sintered at 1373 K in a muffle furnace. Afterwards, the samples for the characterization and the legs for the modules were cut from the pellet and sintered in air with a maximum temperature of 1573 K and a dwelling time of 5 h.

Both materials were characterized in air from room temperature to 1163 K. The Seebeck coefficient (α) and the electrical conductivity (σ) were measured using the Ozawa Science RZ2001i system. The thermal conductivity ($\kappa = \rho \lambda C_p$) was determined using Laser Flash Absorption (LFA; Netzsch LFA 457 Microflash) and a differential scanning calorimeter (DSC; Netzsch DSC 404 C) for the measurement of the thermal diffusivity (λ) and the specific heat (C_p), respectively. For the calculation of κ , the endothermic C_p -peak of the p-type material was excluded. The densities of the samples were determined by the Archimedes method.

A series of four-leg half-skeleton modules (inset of Figure 3) was fabricated from $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$ and $\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_{3-\delta}$. For each module, the total leg cross-sectional area of the four legs was chosen to be $40.77(6) \text{ mm}^2$ with varying cross section ratio ($A_p/A_n = 0.74, 1.01, 1.12, 1.24, \text{ and } 2.74$). The legs were electrically connected by Ag-sheets and joined with a Ag-paste containing 6 wt. % of $\text{Ca}_{2.97}\text{Bi}_{0.03}\text{Co}_4\text{O}_{9+\delta}$ power.^{8,19} The whole module was soldered in air at 1123 K and 6.3 MPa uniaxial pressure.

All generators were characterized in a thermoelectric test stand under identical conditions. The hot-side temperature T_h was measured with two thermocouples fixed on the inner side of the Al_2O_3 plate close to the p- and the n-type legs, while the cold side thermocouples were placed between the silver contact of the p/n-type leg and the cooling plate. Current-voltage characteristics were recorded at different temperature differences using a Keithley2440 SourceMeter (4-wire mode). Independent of the A_p/A_n ratio all modules should supply the same open circuit voltage $V_{OC} = \int_{T_c}^{T_h} \alpha(T) dT$ for the same T_h and T_c . To compensate for small temperature drifts, the power output was extracted from an extrapolation of the measured $P - V_{OC}$ -dependency to the same V_{OC} for all converters (cf. Section I in supplementary material³⁴). In Table I, V_{OC} and the corresponding T_h and T_c measured for the module with $A_p/A_n = 1.12$ are presented for different heater temperatures. Finally, the module efficiencies were calculated using the theoretical total heat flow entering the legs at the hot side. Here, the flow was calculated from the materials' properties, the leg dimensions, and the measured T_c and T_h via Eq. (4), using u or Φ optimized for maximum power output.

TABLE I. Temperature of hot T_h and cold side T_c with corresponding V_{OC} measured for the module with $A_p/A_n = 1.12$.

T_h (K)	369	464	563	658	759	856	949	1051
T_c (K)	297	300	303	308	310	315	321	324
V_{OC} (V)	0.030	0.071	0.115	0.161	0.210	0.259	0.310	0.364

The contact resistivity ρ_c of the oxide-Ag composite (6 wt. % $\text{Ca}_{2.97}\text{Bi}_{0.03}\text{Co}_4\text{O}_{9+\delta}$) interface was determined on series of 7 legs with equal cross section but variable length. Ag contacts were joined to the legs with the same soldering procedure used for the modules. Additionally, a series of $\text{Ca}_{2.97}\text{Bi}_{0.03}\text{Co}_4\text{O}_{9+\delta}$ legs was soldered without pressure (5 h at 1123 K). The length (l) of the legs was determined prior to soldering. The leg resistances R_{tot} were measured in 4-probe geometry with both clamps connected to the supply leads. As $R_{tot}(l) = R_{leg}(l) + 2R_{contact}$ changes linear with l the contact resistance R_c , and thus, the resistivity $\rho_c = R_c A$ can be extracted from a fit.

IV. RESULTS AND DISCUSSION

The materials' properties of both oxides were investigated to understand the dependency of the generator efficiency on the A_p/A_n ratio via theoretical calculations and to fabricate generators with reasonable A_p/A_n ratios. The misfit-layered cobaltite $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$ and the perovskite-type manganite $\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_{3-\delta}$ exhibit 99% ($4.63(10) \text{ g/cm}^3$) and 97% ($4.52(18) \text{ g/cm}^3$) of the theoretical densities,³⁵ respectively. The electrical conductivity, the absolute Seebeck coefficient, and the thermal conductivity of the two oxides are of comparable magnitude (Figures 1(a)–1(c)). For both materials, the experimental data are in agreement with literature,^{28,29} although for the cobaltite κ is in the upper region of the literature values as the measurement direction is across the aligned particles.³⁶ Because of the higher σ at elevated temperatures, the Figure of merit $ZT = \frac{\alpha^2 \sigma}{\kappa} T$ of the p-type material is superior to that of the n-type material (Figure 1(d)). The $\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_{3-\delta}$ samples reached a peak value of $ZT = 0.11$ at 1123 K, which is comparable with other substituted manganites.²⁸ At the same temperature, the $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$ sample reached a $ZT = 0.17$, which is in agreement with the smaller values reported in literature.²⁸

Additionally, in Figure 1(e), the compatibility factors $s(T)$ of the oxides are presented, with s_p showing the stronger temperature dependence. In comparison, the most efficient reduced current densities $u_p^*(T)$ and $u_n^*(T)$ calculated for $\Delta T = 1051 \text{ K} - 324 \text{ K}$ show a relatively flat temperature rise. Because J is constant within the legs, and the conductive heat flows change moderately, the slope of both u is rather small.

To allow both legs to work with the most efficient reduced current densities u_p^* and u_n^* , the ratio of the cross section areas should be equal to $(A_p/A_n)^*$ (see Eq. (2)). In Figures 2(a) and 2(b), this cross section ratio and the corresponding p-n-couple efficiency η_{p+n}^* are presented for different T_h and T_c . Here, η_{p+n}^* illustrates the potential of this

FIG. 1. Thermoelectric properties of $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$ (p-type) and $\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_3$ (n-type): (a) electrical conductivity σ , (b) absolute Seebeck coefficient $|\alpha|$, (c) thermal conductivity κ , (d) Figure of Merit ZT , and (e) compatibility factor s with most efficient reduced current densities for $\Delta T = 1051 \text{ K} - 324 \text{ K}$. Based on the uncertainties in the distance measurement between the electrode-contact wires and the sample dimensions as well as non-optimal thermal contacts, uncertainties of $\Delta\sigma = 7\%$ and $\Delta\alpha = 5\%$ are expected.³⁷ Error propagation of the uncertainties of the density, the thermal diffusivity ($\Delta\lambda = 2\%$), and the heat capacity ($\Delta C_p < 5\%$) results in uncertainties of $\Delta\kappa = 5.5\%$ and $\Delta ZT = 13.4\%$ (error bars are omitted for the sake of clarity).

material composition for different ΔT , giving a maximum value of 1.48% at $\Delta T = 1148 - 298 \text{ K}$. The ratio $(A_p/A_n)^*$ tends to decrease with increasing T_h and T_c (Figure 2(a)). For a thermoelectric generator, the A_p/A_n ratio is fixed and can only be adjusted to a single ΔT . A series of generators was fabricated to investigate the influence of a non-adjusted A_p/A_n ratio on the module performance. Their ratios are presented in Figure 2(c) in comparison with the $(A_p/A_n)^*$ -ratios calculated for the experimentally applied ΔT . The ratios 1.12 and 1.24 are equal or close to $(A_p/A_n)^*$ between 370 and 660 K, whereas the ratio 1.01 is adjusted to T_h around 920 K.

FIG. 2. Cross section area $(A_p/A_n)^*$ ensuring the highest efficiencies of both legs (a) and maximum efficiency η_{p+n}^* of a generator with ratio $(A_p/A_n)^*$ for different cold T_c and hot side temperatures T_h (b). Additionally, $(A_p/A_n)^*$ for the used experimental T_h and T_c are shown in comparison with the ratios of the fabricated generators (lines) (c).

FIG. 3. Room temperature module resistances R^{exp} measured for different A_p/A_n ratios (black circles) with corresponding fit of $R_{\text{av}}^{\text{calc}}(A_p/A_n)$ (Eq. (5)). Additionally, the module resistances R^{calc} calculated from the leg dimensions and resistivities are presented (squares). The red line shows the resistance $R_{\text{av}}^{\text{calc}}(A_p/A_n)$ calculated for the average module area and leg height. For R^{calc} , an additional contribution from the contact resistance smaller than $4 \text{ m}\Omega$ has to be considered. In the inset, a picture of the fabricated 4-leg generators is presented.

In contrast, the ratios 0.74 and 2.74 are smaller or much larger than $(A_p/A_n)^*$, respectively.

A picture of the fabricated modules and the measured room temperature resistances R^{exp} are presented in Figure 3. A minimal value of $152.12 \text{ m}\Omega$ was found for $A_p/A_n = 1.24$. This is about 7% larger than the room temperature resistance R^{calc} calculated from the geometry of the four generator legs connected in series. As a guide for the eye, the continuous function

$$R_{\text{av}}^{\text{calc}}\left(\frac{A_p}{A_n}\right) = 2(R_n + R_p) = 2 \frac{d}{A_p + A_n} \left(\frac{1}{\sigma_n} \left(1 + \frac{A_p}{A_n} \right) + \frac{1}{\sigma_p} \left(\frac{1}{\frac{A_p}{A_n}} + 1 \right) \right) \quad (5)$$

is plotted, which describes the summarized room temperature resistances for the p- and the n-type legs R_p and R_n with varying A_p/A_n using the constant average leg height $d = 0.411(4) \text{ cm}$ and the constant average $A_p + A_n$ of all modules (Figure 3). The very small discrepancy between the average function $R_{\text{av}}^{\text{calc}}$ and R^{calc} emphasizes the

precise cutting of the leg geometry and the homogeneity of the material.

Additionally, the contact resistances of the oxide-Ag interfaces are expected to contribute to R^{calc} . For $\text{CaMn}_{0.97}\text{W}_{0.03}\text{O}_{3-\delta}$, a contact resistivity of $\rho_p^c = 0.04(2) \text{ m}\Omega \text{ cm}^2$ was found for a series of legs soldered in the same way as the modules. As the contact resistivity of the $\text{Ag-Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$ contacts soldered this way is too small for a reliable determination, it was determined for a $\text{Ag-Ca}_{2.97}\text{Bi}_{0.03}\text{Co}_4\text{O}_{9+\delta}$ -interface soldered without pressure. Here, a contact resistivity of $\rho_p^c = 0.025(16) \text{ m}\Omega \text{ cm}^2$ was found. Adding the contacts resistances leads to contact resistance of about $R_c = 4 \text{ m}\Omega$ per generator. Because this value amounts to only about 2% of the total module resistance, its omission in the theoretical calculations is reasonable. The observed difference between R^{calc} and R^{exp} does not result from the contacts, but a change of the resistance of the p-type material during the hot pressing of the module is observed (cf. Section II in supplementary material³⁴).

The measured power outputs of the fabricated generators is presented in Figures 4(a) and 4(b) to analyze the effect of the A_p/A_n ratio. While only the absolute power outputs $P_{1.01}$ and $P_{2.74}$ of the generators with $A_p/A_n = 1.01$ and 2.74 are depicted in Figure 4(a), small differences between all the generators are displayed in Fig. 4(b) via a normalization to $P_{1.01}$. Depending on the A_p/A_n ratio, different temperature dependencies are observed, although the power outputs of all generators increase with T_h (or ΔT). For T_h around 400 K, the highest power outputs (1.45 mW) are produced by generators with the ratios 1.12 and 1.24, whereas the ratios 1.12 and 1.01 are most suitable for T_h around 1051 K ($P_{max} =$

200.4 mW). In contrast, a strong reduction of the power output is observed for the ratios 0.74 and 2.74, which differ strongly from $(A_p/A_n)^*$. At the largest ΔT , a reduction of up to 23% is found for $P_{2.74}$ compared to $P_{1.01}$.

To better understand the observed trends, the theoretical power outputs are calculated based on the measured T_h and T_c as well as the materials properties (Figures 4(c) and 4(d)). Additionally, for every T_h , the theoretical power output of a module with the ratio $(A_p/A_n)^*$ is depicted. The theoretical power output exceeds the experimental ones by up to 35%. However, the model describes the relative changes very well (compare Figures 4(b) and 4(d)). In agreement with the experimental values, it predicts the strongly reduced power outputs for the ratios 0.74 and 2.74. Furthermore, it also confirms that the highest power outputs are produced for the ratios 1.12 and 1.01 in the low- and the high-temperature regions, respectively. Comparing the power outputs with the one of $(A_p/A_n)^*$, it can be concluded that the closer A_p/A_n is to $(A_p/A_n)^*$ the higher is the power output (cf. Figure 2(c)).

This dependency of the power output on the A_p/A_n ratio can be understood by having a closer look at the reduced current densities within the legs. In line with the introduced theoretical model, we will use the symbols u_p^* and u_n^* for the reduced current densities, leading to the highest leg efficiencies and the symbols u_p^{**} and u_n^{**} for the reduced current densities that lead to the highest efficiency of the entire generator. The total efficiency of one leg is calculated from the reduced efficiency $\eta_r(u)$, which reaches to a maximum value $\eta_{r,max}$ for $u = s$. While the slope of the compatibility factor $s(T)$ is fixed by the material properties of the two oxides, the slope of $u(T)$ is determined by the heat equation, cf. Figure 5(a). The highest leg efficiency is reached for the u^* , which is closest to s within the whole temperature range. For a generator with $(A_p/A_n)^*$, this is the case for both legs, but for different ratios, u_p^{**} and u_n^{**} differ from u_p^* and u_n^* . This is illustrated in Figures 5(a) and 5(b). For a generator with ratio $A_p/A_n = 1.01$, the η_r and u^{**} nearly coincide with

FIG. 4. Temperature dependent experimental power outputs for $A_p/A_n = 1.01$ and 2.74 (a). A normalization of the experimental power outputs to the power output measured for the generator with $A_p/A_n = 1.01$ reveals also small differences between the different ratios (b). In comparison to the experimental values (open symbols), the corresponding theoretical values (filled symbols) are presented in (c) and (d). Additionally, the values of a generator with $(A_p/A_n)^*$ adapted to each temperature difference are shown.

FIG. 5. (a) Local reduced efficiency η_r normalized to the maximum reduced efficiency $\eta_{r,max}$ of the material with (b) corresponding reduced current densities u^* and compatibility factors s calculated for $\Delta T = 1133 \text{ K} - 293 \text{ K}$.

the values of a generator with $(A_p/A_n)^* = 0.96$. In contrast, for $A_p/A_n = 2.74$, the u_p^{**} and u_n^{**} deviate strongly from u_p^* and u_n^* and $\eta_r/\eta_{r,max}$ is reduced by up to 43% and 73% for the p- and the n-leg, respectively. A closer look reveals that for the p-type leg the highest efficiency losses are observed at high T , where the ratio u_p^{**} between electrical current density and heat flux is smaller than s_p . Accordingly, the thermoelectric segment produces a Seebeck voltage, but the electrical current is much smaller than for $u = s$. Thus, the efficiency and the power output, which increase linearly with the current, are small. For the n-type leg, the efficiency is also reduced, but in this case, u_n^{**} is larger than s_n . Here, the decrease results from Joule heating that is proportional to the square of the current and thus more dominant for higher values. Consequently, the two legs cannot work efficiently at the same time, because for a given u_n^{**} , the reduced current u_p^{**} is fixed by the A_p/A_n ratio and thus in at least one leg the reduced current is unfavorable.

For the largest temperature difference $\Delta T = 727$ K, the highest experimental power output is reached for the module with the ratio $A_p/A_n = 1.12$ (cf. Figure 4). The measured maximum power output, the maximum power density normalized to the total cross-sectional area of the legs, the leg volume, and the mass of the thermoelectric legs are found to be $P_{max} = 200.4$ mW, 0.49 W/cm², 1.2 W/cm³, and 0.26 W/g for $\Delta T = 727$ K and $A_p/A_n = 1.12$, respectively. These values are comparable with values found for other oxide converters.^{7,9,10} The measured volume and area power densities are even 24% and 9% larger than the most promising literature values of 0.96 W/cm³ and 0.45 W/cm² found for a $\text{Ca}_{2.7}\text{Bi}_{0.3}\text{Co}_4\text{O}_9/\text{LaNiO}_3$ generator with similar T_h of 1073 K.¹⁵

The power densities are not the most adequate parameters for a comparison of generator performance since they depend on the height of the legs (l_{tot}). Informative is the calculation of the Figure of Merit $Z_M = \frac{4P_{max}}{K\Delta T^2}$ of the module,³⁸ where K is the thermal conductance $K = \frac{N}{l_{tot}}(\bar{\kappa}_n A_n + \bar{\kappa}_p A_p)$, N the number of p-n couples, and $\bar{\kappa}_n$ and $\bar{\kappa}_p$ the average values of the conductivities at the hot and the cold side of the legs. For the $A_p/A_n = 1.12$ module at the highest applied temperature, a value of $Z_M = 52/\mu\text{K}$ was calculated.

The efficiency calculation allows the direct estimation of the power output for a given heat flow, which is an important value for the application. The heat flow is calculated from the measured $T_h = 1051$ K and $T_c = 324$ K, the leg dimensions and the materials properties via Eq. (4). However, T_h seems to overestimate the actual temperature, because it was measured on the Al_2O_3 -plate next to the legs. The measured open circuit voltage ($V_{OC} = \int_{T_c}^{T_h} \alpha(T) dT$) leads to a value of $T_h^{V_{OC}} = 970$ K, which is about 8% smaller than T_h . This difference might originate from the active cooling of the legs, which has only a small effect on T_h . For the generator with $A_p/A_n = 1.12$ for T_h , a total heat flow of $Q_{tot} = 22.0$ W and an experimental converter efficiency of $\eta_{p+n}^{T_h} = 0.91\%$ are found. In contrast, for $T_h^{V_{OC}}$, a heat flow of $Q_{tot} = 19.7$ W is calculated, and the measured efficiency reaches an even higher value of $\eta_{p+n}^{T_h^{V_{OC}}} = 1.02\%$.

For the same T_h and $T_h^{V_{OC}}$, a detailed overview on the change of the experimental and the theoretical couple efficiency with the A_p/A_n ratio is given in Figure 6. As discussed for the power output, also the generator efficiency decreases dramatically (up to 23%) for A_p/A_n deviating strongly from $(A_p/A_n)^*$. Experimental and theoretical values show a similar A_p/A_n dependency. For T_h , the experimental efficiencies stay up to 25% below the theoretical values. In contrast, if the heat flow and the theoretical power output are calculated for $T_h^{V_{OC}}$, the difference between the theoretical and the experimental efficiencies is smaller than 3%. Thus, $T_h^{V_{OC}}$ seems to be the more reliable temperature.

From the theoretical calculations, it can be seen that $(A_p/A_n)^*$ does not lead to the maximum efficiency of the whole module, but it is obviously very close to it (Figure 6): compared to the optimal ratio for T_h , a 0.04% higher efficiency is found for an increase of the cross section area by 6%. This can be explained by the definition of the generator efficiency (Eq. (3)). A change of the A_p/A_n ratio changes the total heat flow and more important the weighting of the p- and the n-leg efficiency that determines the power output $P = \eta_p Q_p^h + \eta_n Q_n^h$. For $A_p/A_n > (A_p/A_n)^*$, the larger A_p increases the heat flow $Q_p = J_p \Phi_p A_p$ through the p-leg with the higher efficiency (η_p), whereas Q_n decreases with A_n . Additionally, the leg efficiencies of one or both legs decrease because $u_n \neq u_n^*$ or $u_p \neq u_p^*$. In case that the change of the heat flows dominates the change of leg efficiency, this can lead to a higher power output. Accordingly, higher values can be reached through A_p/A_n ratio different from $(A_p/A_n)^*$, although the efficiencies of the single legs are smaller. Regarding the efficiency, it has to be considered that an increase of A_p/A_n leads to a higher heat flow $Q = Q_p + Q_n$ for the same ΔT , due to different Φ of the legs. Thus, it is possible that maximum efficiency and maximum power can be found at slightly different ratios. However, this difference is considered to be rather small.³⁹

FIG. 6. Experimental (filled) and theoretical converter efficiency (open symbols) for the fabricated and additional A_p/A_n ratios for $T_c = 324$ K. For the calculation of the heat flow and the efficiency, either the measured T_h or the estimated temperature $T_h^{V_{OC}}$ was used. For both temperatures, $(A_p/A_n)^*$ is shown (stars). As radiative losses are neglected, η_{p+n} is overestimated by about 8% (cf. Section III in supplementary material³⁴).

For the presented material combination, the most efficient ratio is close to $A_p/A_n = 1$, but for material combinations with very different properties, this commonly used ratio may result in a tremendous decrease of the efficiency. Thus, a fast calculation of the most efficient ratio according to Eq. (2) is highly recommended prior to generator fabrication. Furthermore, around the maximum efficiency the curve is relatively flat (Figure 6). This offers the opportunity for cost weight or volume reduction without remarkable efficiency losses, which is of particular importance for mobile applications, e.g., in the automotive industry.

Finally, the long-term stability of the generator with $A_p/A_n = 1.12$ is investigated for 114 h (Figure 7) for the final application on a casting furnace at vonRoll casting. The test is performed at $T_h \approx 1160$ K and $T_c \approx 355$ K. Although T_h is close to the decomposition temperature (1200 K) of the cobalt oxide²⁷ and the melting point of silver (1235 K), no degradation effects are observed. The internal resistance R_i of the generator is constant (Figure 7(d)), which points out the long time stability of the Ag-contacts achieved by intermixing with the oxide powder. The maximum power output reaches a peak value of 237 mW and varies by about 2%. This variation is probably induced by the 3% variation of ΔT , which also reflects in a change of V_{OC} . Normalization of the maximum power output to the total cross-sectional area of the legs, the leg volume, and the mass of the thermoelectric legs lead to values of 0.58 W/cm², 1.4 W/cm³, and 0.31 W/g, respectively. This power corresponds to a maximum efficiency of 0.99% for the measured T_h and 1.08% if the more reliable estimated $T_h^{V_{OC}} = 1085$ K is used for the calculation of the heat flow.

FIG. 7. Stability of the generator with $A_p/A_n = 1.12$ during 114 h of energy conversion. The maximum power output (a), the open circuit voltage (b), and the internal resistance (c) are constant. Small variations might result from small drifts of the hot (d) and the cold side temperature (e).

V. CONCLUSION

A series of four-leg thermoelectric modules with varying A_p/A_n ratio was fabricated, characterized, and successfully tested in long-term tests at very high temperatures. It was shown that the power output and the efficiency of the thermoelectric generators increase strongly for an adjustment of the cross section ratio A_p/A_n according to the compatibility approach. For A_p/A_n differing strongly from $(A_p/A_n)^*$, a relative decrease of the experimental efficiency of up to 23% was observed. For the best performing module with $A_p/A_n = 1.12$, the long-term thermal stability was demonstrated, which highlights the reliability and the potential of the oxide thermoelectric converters for high temperature applications. The measured maximum power output, the maximum power density normalized to the total cross-sectional area of the legs, the leg volume, and the mass of the thermoelectric legs were found to be 237 mW, 0.58 W/cm², 1.4 W/cm³, and 0.31 W/g, respectively. Based on the measured temperature $T_h = 1160$ K and the smaller estimated $T_h^{V_{OC}} = 1085$ K, the calculated heat flow leads to efficiencies of 0.99% and 1.08%, respectively. Theoretically, even higher efficiencies are possible since for $\text{Ca}_3\text{Co}_{3.9}\text{O}_{9.3+\delta}$ higher ZT were reported in literature.

Despite its simplifications, the theoretical compatibility model describes the experimental trends very well and offers an easy way for the improvement of thermoelectric converters. Especially, the calculated dependency of the efficiency on the A_p/A_n ratio can be used for cost, weight, and volume reduction, which is crucial for large-scale applications of thermoelectric converters for waste heat recovery.

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