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ARTICLE

Long-term stability of phase-separated Half-Heusler compounds

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J. Krez A,^{a,b} B. Balke,^{a,*} S. Ouardi,^c S. Selle^d, T. Höche^d, C. Felser,^c W. Hermes^e and M. Schwind^e

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Half-Heusler (HH) compounds have shown high figure of merit up to 1.5. Here, we address the long-term stability of *n*- and *p*-type HH materials. For this purpose, we investigated HH materials based on the Ti_{0.3}Zr_{0.35}Hf_{0.35}NiSn-system after 500 cycles (1700 h) from 373 to 873 K. Both compounds exhibit a maximum Seebeck coefficient of $|\alpha| \approx 210 \mu\text{VK}^{-1}$ and a phase separation into two HH phases. The dendritic microstructure is temperature resistant and upon cycling the changes in the microstructure are so marginal that the low thermal conductivity values ($\kappa < 4 \text{ Wm}^{-1}\text{K}^{-1}$) could be maintained. Our results emphasize that phase-separated HH compounds are suitable low cost materials and can lead to enhanced thermoelectric efficiencies beyond the set benchmark for industrial applications.

1. Introduction

The search for alternative energy technologies has intensified in recent years as climate change has become more noticeable and the usage of nuclear energy introduces political controversy for many countries. The challenge here lies in developing sustainable energy conversion techniques that can compete with the efficiency of fossil fuels. In terms of waste heat recovery, thermoelectric generators (TEG) provide an excellent method for generating electricity from dissipated heat.^{1,2} Especially in the automobile industry, TEGs play a crucial role in decreasing greenhouse gas emissions and fuel consumption.³ For commercial and versatile application of TEG in power generation, thermoelectric (TE) materials need to meet several criteria besides high efficiency, such as environmentally friendliness, low cost production and long-term thermal stability. The TE efficiency of a given material is determined by the dimensionless Fig. of merit zT as given in Equation (1):

$$zT = \frac{\alpha^2 \sigma}{\kappa} T, \quad (1)$$

where α is the Seebeck coefficient, σ the electrical conductivity, and κ the total thermal conductivity.¹

The general strategy towards high TE efficiency can be attained by enhancing the electronic properties through optimization of the carrier concentration and by reducing the thermal conductivity through effective phonon scattering^{1,2}. Slack introduced the “phonon-glass electron crystal” concept and showed that there is a limitation of zT , since the required materials properties, such as high electrical conductivity and low thermal conductivity, are strongly related to each other.⁴ Assuming that the total thermal conductivity κ has just an electronic contribution (κ_{el}) and a lattice contribution (κ_{lat}) one can use the Wiedemann–Franz law $\kappa_{el} = L \sigma T$ (L is the Lorentz number) to calculate this two different contributions to the thermal conductivity.

Most current research on high- zT TE materials is focused on introducing nanostructures or nanoinclusions to minimize κ_{lat} and therefore, to minimize the total thermal conductivity;^{5,6} however, it is doubtful whether the criteria of reproducibility and thermal stability

are met by nanostructured materials especially under operating at high temperatures.⁷ Intermetallic HH compounds with a general formula XYZ (X, Y = transition metals; Z = main group element like Sn or Sb) have attracted considerable attention as suitable TE materials because of their very flexible electronic structure (band gap tunability from zero to 4 eV)⁸ and high Seebeck coefficients ($|\alpha| > 200 \mu\text{VK}^{-1}$).^{6,9–13} Thereby, the transport properties can easily be changed from *n*-type to *p*-type behavior by electronic doping with non-isoelectronic elements.^{6,14} Thus, donor impurities (elements with higher valence electron count) lead to a shift of the Fermi energy towards the conduction band (higher energies), while acceptor impurities (elements with higher valence electron count) will shift the Fermi energy into the valence band (lower energies). Furthermore, multi-component HH compounds exhibit an intrinsic phase separation during their solidification process¹⁵ and they exhibit high melting points ($> 1400 \text{ K}$).¹⁶ Temperature stable microstructures can establish an entirely new area of research, where the phase-separation microstructure can be independently engineered to fulfill desired TE properties,⁴ leading to further improvements in TE efficiencies beyond the current state-of-the-art materials.

Numerous studies investigated the TE properties of multi-component MNiSn- and MCoSb-based HH materials.^{6,11,17} Thereby, zT values up to 1.5 for *n*-type materials⁹ and 1.0 for *p*-type materials¹¹ could be attained. However, to the best of our knowledge, there are no reports on the importance of the long-term stability of HH compounds or the preservation of their TE properties through repeated heating and cooling. Very recently, Bartholomé *et al.* investigated the reproducible up-scaling process of *n*-type Zr_{0.4}Hf_{0.6}NiSn_{0.98}Sb_{0.02} and *p*-type Zr_{0.5}Hf_{0.5}CoSb_{0.8}Sn_{0.2} into kilogram batches.¹⁸ The TE module comprising these HH compounds contained 7 *n*- and 7 *p*-type legs and exhibited a maximum power output of 2.8 W. This work presents the first study on the long-term stability of phase-separated (Ti,Zr,Hf)NiSn HH compounds. The exemplary *n*-type Ti_{0.3}Zr_{0.35}Hf_{0.35}NiSn and *p*-type Ti_{0.26}Sc_{0.04}Zr_{0.35}Hf_{0.35}NiSn HH compounds were subjected to 500 heating-cooling cycles from 373 to 873 K, lasting about 1700 h. The TE properties were measured after 50, 100, and 500 cycles up to 900 K.

2. Experimental

The samples $\text{Ti}_{0.3-x}\text{Sc}_x\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ ($x=0$ and 0.04) were prepared by arc melting of Ti, Sc, Zr, Hf, Ni, Sn (purity of all elements was 99.9%) in a purified argon atmosphere using a mixture of stoichiometric amounts of these elements. To ensure homogeneity, the samples were re-melted several times. The as-cast samples were annealed at 1223 K for 7 days in order to improve the crystalline order, and this was followed by quenching in ice water. The samples were cut into rectangular bars and discs, which were used later for characterization and thermoelectric properties measurements. Subsequently, they were placed in quartz ampules under vacuum and subjected to a temperature profile from 373 K up to 873 K with a heating/cooling rates of 10 K/min. Fifty cycles of temperature increase/decrease lasted approximately 170 h including the holding time of 90 min at 600 °C in each cycle.

Powder X-ray diffraction (PXRD) measurements were performed with Cu K α radiation at room temperature, using an image-plate Huber G670 Guinier camera equipped with a Ge(111) monochromator. The microstructures characterization of the samples were examined by scanning electron microscopy (SEM) using a Philips X scanning electron microscope. Quantitative electron probe microanalysis (EPMA) of the phases was carried out by using a wavelength energy dispersive X-ray (EDX) analyzer (Phoenix V 5.29, EDAX) and a wavelength-dispersive spectrometer (Cameca SX 100) with the pure elements as standards (the acceleration voltage was 25 kV, using the K- and L-lines).

In addition, samples were analyzed by High Resolution Transmission Electron Microscopy (HRTEM). A thin lamella was cut from the samples via focused ion beam machining (FIB).

The electrical conductivity σ and Seebeck coefficient α were measured simultaneously under a helium gas atmosphere from room temperature up to about 900 K using a Linseis LSR-3 system. Heating and cooling cycles yielded repeatable electrical properties for a given sample. The thermal conductivity κ was evaluated as a product of the thermal diffusivity D , heat capacity c_p , and measured density ρ . The thermal diffusivity D was measured by a laser flash method using the Netzsch LFA 457. The electron contribution to the thermal conductivity is calculated from the electrical conductivity measurement results using the Wiedemann–Franz Law. All samples were coated with a thin layer of graphite to minimize emissivity errors. The heat capacity c_p was measured by differential scanning calorimetry using the Netzsch STA 449. The density was determined via a geometrical method by measuring the weight and dimensions of the rectangular bars before and after the thermal treatment. The uncertainties were 3% for the electrical conductivity, 5% for the Seebeck coefficient, and 3% for the geometrical density measurements, the thermal diffusivity and the heat capacity measurement, thereby leading to a 5.2% uncertainty in thermal conductivity, and 11.66% in the ZT values.

3. Results and discussion

The crystalline structure of the compounds was determined by powder X-ray diffraction (PXRD) measurements. The obtained X-ray patterns reveal a cubic C1_b structure ($\text{F}\bar{4}3\text{m}$), which is in agreement with results found in the literature¹⁹. Splitting of the Bragg reflection peaks – as shown in the inset of Fig. 1 – is caused by the coexistence of two or more HH phases. During the solidification process, the multi-component HH system dissipates into a main Ti-poor (HH 1) phase and a Ti-rich (HH 2) phase¹⁵. The lattice parameters (derived by Rietveld analysis) of both n -type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ and p -type

$\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ HH compounds are listed in Table 1. According to the 4% Sc substitution and larger radius of Sc (Ti 140 pm, Sc 160 pm), the lattice constant is higher for the p -type material, indicating that Sc substituted into the Ti lattice.

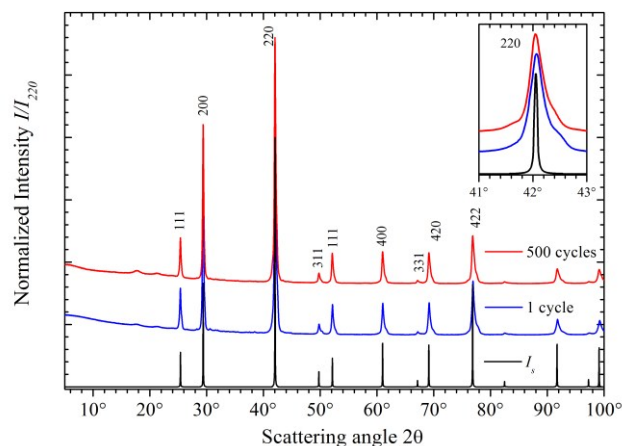


Fig. 1: Figure X: PXRD of the n -type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$. Displayed are the simulated pattern (I_s), experimental patterns of annealed sample (1 cycle) and the sample after 500 cycles. Reflections are indexed according to the half-Heusler structure $\text{F}\bar{4}3\text{m}$.

Table 1: Lattice parameters and chemical compositions determined using energy dispersive X-ray analysis of phase-separated n -type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ and p -type $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ HH compounds.

	Lattice parameter a [Å]	Composition
$\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ (n-type)		
Ti-poor phase (HH 1)	6.068(2)	$\text{Ti}_{0.18}\text{Zr}_{0.40}\text{Hf}_{0.41}\text{NiSn}$
Ti-rich phase (HH 2)	6.012(3)	$\text{Ti}_{0.65}\text{Zr}_{0.2}\text{Hf}_{0.17}\text{NiSn}$
$\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ (p-type)		
Ti-poor phase (HH 1)	6.071(7)	$\text{Ti}_{0.14}\text{Sc}_{0.04}\text{Zr}_{0.4}\text{Hf}_{0.41}\text{NiSn}$
Ti-rich phase (HH 2)	6.045(6)	$\text{Ti}_{0.62}\text{Sc}_{0.04}\text{Zr}_{0.20}\text{Hf}_{0.17}\text{NiSn}$

The backscattering electron mode (BSE) SEM images of the n - and p -type samples before and after 500 cycles, shown in Fig. 2, revealed the intrinsic phase separation into the main Ti-poor HH 1 phase and the Ti-rich HH 2 phases, which is dendritically interlaced as seen in the corresponding microstructure. The compositions of the phases for the n - and p -type HH compounds are listed in Table 1. In case of p -type HH, a Sc substitution yield to a homogenous distribution of Sc (4%) in both phases. The resulting phase separation is stable under the cycling conditions – the phase boundaries of the dendrites are even more pronounced – which is of utmost importance for maintaining low thermal conductivities in these HH materials.

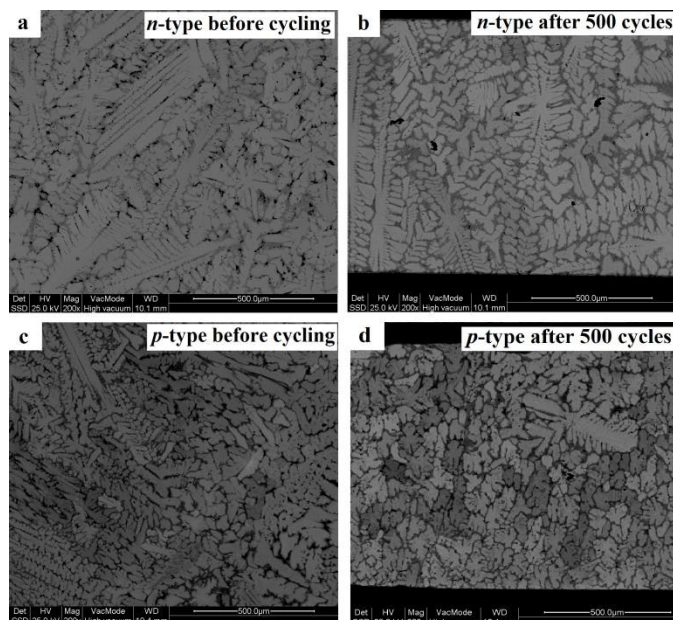


Fig. 2: SEM images of the *n*-type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ and *p*-type $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ HH compound. a) *n*-type compound before cycling. b) *n*-type compound after 500 cycles. c) *p*-type compound before cycling. d) *p*-type compound after 500 cycles.

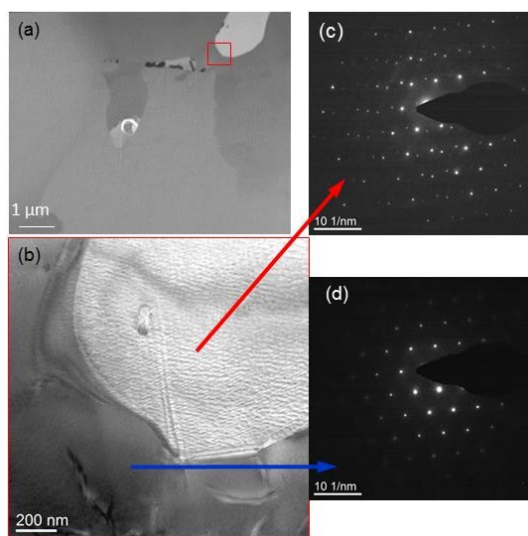


Fig. 3: TEM and electron diffraction (ED) images of *p*-type $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ compound after 500 cycles. (a) shows a TEM overview of the sample and (b) shows a HRTEM image of an area where all phases could be observed. (c) and (d) show the ED images of the 2nd phase and the main phase (HH1), respectively.

Fig. 3 shows the image of the FIB lamella prepared from the 500 cycled $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ sample (Fig. 3(a)) and the HRTEM image (Fig. 3(b)). Figs. 3(c) and 3(d) show the electron diffraction (ED) of selected area from each phase. ED of the main phase (HH1) shows that the grains are single crystals, while the splitting of the diffraction spots from second phase confirmed the coexistence of different HH phases (HH2 plus at least one other phase which could not be resolved neither in the SEM data nor in the XRD data) in nano-composites scale.

The transport properties of the semiconducting *n*-type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ HH system were measured up to 873 K after 500 cycles (1700 h) (see Figure 4). The electrical conductivity σ improved after 50 cycles due to an enhancement of the structural order (see Figure 4(a)).⁶ The Seebeck coefficient α is negative at all temperatures, indicating electrons as the majority charge carriers, with a peak value of $\alpha \approx -210 \mu\text{V/K}$ at 600 K (see Figure 4(b)). The large Seebeck coefficient emerges from the high density of states, which is caused by the *d*-states of the transition metals near the Fermi level.¹⁹ The decrease in α above 600 K is caused by the thermal excitation of intrinsic carriers. The power factor PF shows a peak value of $2.5 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at 773 K after 50 cycles which is comparable to values of *n*-type Bi_2Te_3 , i.e., $PF \sim 2.6 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at 423 K.²⁰ A recent investigation of the long-term efficiency of a commercial available bulk- Bi_2Te_3 TEG with 31 thermocouples showed a reduction in α and σ caused by material deterioration.²¹ The thermal conductivity κ of (Ti,Zr,Hf)NiSn compounds is much lower than of ternary HH alloys, where $\kappa > 7\text{--}17 \text{ Wm}^{-1}\text{K}^{-1}$.²² The low κ values of the phase-separated HH system occur due to the scattering of phonon of several different frequencies. The impedances of high-frequency phonons are induced by alloy scattering, while low and mid-frequency phonons are effectively scattered at the dendritic interfaces.²³ Owing to the improved structural order of the *n*-type compound, κ increases slightly after 500 cycles (see Figure 4(c)). The increase in κ above 600 K is caused by the excitation of intrinsic carriers.

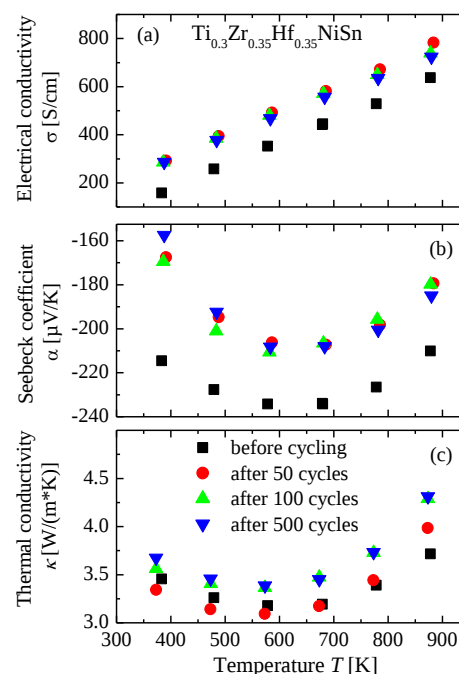


Fig. 4: Thermoelectric properties as a function of temperature of the *n*-type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ compound under the long-term treatment for 500 cycles. a) Electrical conductivity $\sigma(T)$, b) Seebeck coefficient $\alpha(T)$, c) Thermal conductivity $\kappa(T)$.

The substitution of 4% Sc on the (Ti,Zr,Hf)-site in the *n*-type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ parent compound leads acceptor impurities, shifting the Fermi level into the valence band, resulting in *p*-type conductivity for the $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ compound. The temperature dependence of the electrical conductivity σ shows a metallic-like behavior (see Figure 5(a)). The σ values for the *p*-type are lower than those for the *n*-type, caused by the diminished mobility of carriers due to the shift of the Fermi level into the heavier valence band⁶. The Seebeck coefficient α is positive over the entire

temperature range, reaching a maximum of $\alpha \sim 210 \mu\text{VK}^{-1}$ at 600 K (see Figure 5(b)), which is the highest reported value for a *p*-type material based on a (Ti,Zr,Hf)NiSn system.¹⁹ Both *n*- and *p*-type HH compounds exhibit equally high Seebeck coefficients within the same temperature range. The decrease in the absolute Seebeck coefficient α for both systems above 600 K arises from the onset of minority carrier activation. The thermal conductivity κ is further reduced for the *p*-type compound ($\kappa \sim 2.5 \text{ Wm}^{-1}\text{K}^{-1}$) below 600 K (see Figure 5(c)), owing to alloy scattering resulting from the 4% Sc substitution.²⁴

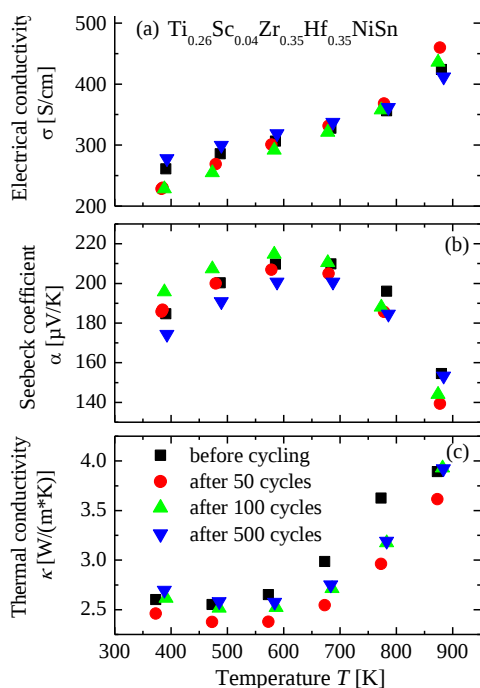


Fig. 5: Thermoelectric properties as a function of temperature of the *p*-type $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ compound under the long-term treatment for 500 cycles. a) Electrical conductivity $\sigma(T)$, b) Seebeck coefficient $\alpha(T)$, c) Thermal conductivity $\kappa(T)$.

Figure 6 visualizes the impact of the thermal cycling on the figure of merit zT for both materials. The TE properties exhibit only a weak dependence on the cycling conditions (1700h). First, after 50 cycles the TE properties change a bit but after 100 cycles the performance is quite stable. This results make the HH compounds a very promising materials with long-term stability of the TE properties. In the near future, more and even longer long-term stability test with different temperature profiles of the TE properties but also on the mechanical properties have to be done.

Conclusion

We were able to prove the long-term stability for the two HH materials, the *n*-type $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ and *p*-type $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$. Their thermoelectric properties are stable even after 500 cycles (1700 h) in a temperature range from 373 to 873 K. The figure of merit zT for both *n*- and *p*-type compounds does not change significantly under the long-term treatment. The dendritic microstructure consisting of a Ti-poor HH 1 and a Ti-rich HH 2 phase in both *n*- and *p*-type HHs is stable under the long-term cycling, which is crucial to maintain the low thermal conductivities in the HH materials. This approach involving an induced thermally stable microstructure could be the key for improving the thermoelectric performances of HH compounds above known limits. Our results

strongly demonstrate the suitability of phase-separated HH materials, which also comply with requirements such as reproducibility and environmental friendliness via mechanical and thermal stability, for a commercial TE application at moderate temperature.

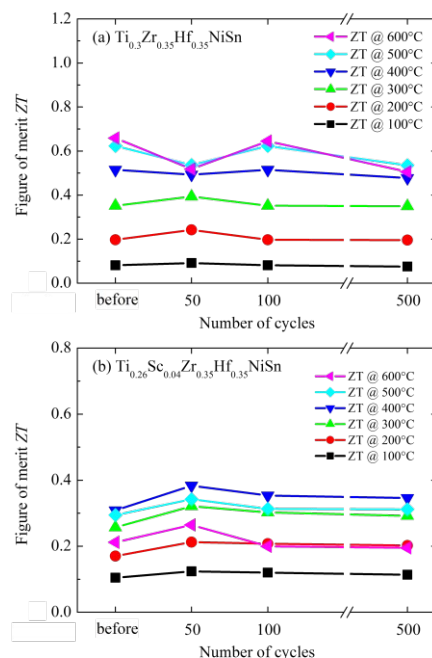


Fig. 6: Figure of merit zT as function of number of cycles for (a) $\text{Ti}_{0.3}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ and (b) $\text{Ti}_{0.26}\text{Sc}_{0.04}\text{Zr}_{0.35}\text{Hf}_{0.35}\text{NiSn}$ - each line represents measurements at constant temperature after the various heat treatment steps (see legend).

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Notes and references

- ^a Dr. J. Krez, Dr. B. Balke, Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, Staudingerweg 9, 55128 Mainz, Germany;
*Dr. B. Balke, Email: balke@uni-mainz.de
- ^b Dr. J. Krez, Graduate School for Excellence Materials Science in Mainz, Johannes Gutenberg University Mainz, Staudingerweg 9, 55128 Mainz, Germany
- ^c Dr. S. Ouardi, Prof. Dr. C. Felser, Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany
- ^d Dr. S. Selle, Dr. T. Höche, Fraunhofer Institut für Werkstoffmechanik, 06120 Halle, Germany
- ^e Dr. Wilfried Hermes, Dr. Markus Schwind, BASF SE, 67056 Ludwigshafen, Germany

*Email: balke@uni-mainz.de

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