Conflicting primary and secondary properties of thermoelectric devices – A case study on the thermomechanical behavior of ZrNiSn

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ABSTRACT
While the primary properties of thermoelectric devices, directly related to the conversion efficiency, are considered in design efforts, the secondary (thermomechanical) properties are often ignored or overlooked even though they can lead to failure. Here, thermomechanical properties of thermoelectric ZrNiSn in the amorphous and crystalline state are studied using density functional theory and two phonon models. Thermal conductivity is also a key primary property for thermoelectric applications. Amorphous ZrNiSn exhibits a fourfold lower thermal conductivity than the crystalline counterpart due to high phonon-phonon scattering, which is conducive to thermoelectric performance. However, this is conflicting since a high thermal conductivity value is required to attain high resistance to thermal shock. Due to stronger bonds in the crystalline counterpart, facilitated by the stronger Zr 3d – Ni 3d and Sn 5p – Ni 3d hybridization and higher coordination than in the amorphous state, the linear coefficient of thermal expansion is lower, and the elastic modulus is higher. Hence, the crystalline state yields higher resistance to thermal shock. It is suggested that samples entailing both amorphous and crystalline regions can concurrently satisfy the primary and secondary requirements for enhanced efficiency and durability.

1. Introduction

Thermoelectric devices convert heat flux directly into electricity without carbon emission [1–3]. This effect was discovered by Thomas J. Seebeck two centuries ago and was named after him [4]. Such devices are in principle heat engines, but they possess no moving parts, making them durable. Due to the relatively low efficiency of commercial thermoelectric devices, their applications are limited to off-grid uses, wearable devices, space probes, satellites, industrial waste heat recovery, as well as cooling, to name a few [1,2]. Unlike other renewable energy sources, thermoelectric devices do not succumb to a supply chain disruption since the thermal gradients in natural and artificial environments are often abundant. Strategies to enhance the thermoelectric efficiency or figure of merit (ZT = S²σ T / κ) at a given temperature (T) include maximizing the Seebeck coefficient (S) and electrical conductivity (σ), while reducing the thermal conductivity (κ) [1,2]. However, these physical properties are conflicting in the way that any improvement of one physical property is often associated with an undesirable effect [1,2]. For example, electrons give rise to electricity (high σ), but they also conduct heat (high κ), which is certainly unwanted in terms of thermoelectric efficiency. There are several approaches to decouple the transport properties. For example, nanostructuring may lead to increased phonon scattering (lower κ) and leave σ less altered so that ZT can be enhanced [1,2]. Another interesting notion has been introduced by Nolas and Goldsmid [5]. They have suggested that phases with the phonon mean free path larger than that of charge carriers (electrons or holes) can exhibit a high ZT value, which may be accomplished in amorphous solids [5]. ZrNiSn [6], ZnO [7], In-Ga-Zn-O [8], NbO₂ [9], and TiO₂-PbO-V₂O₅ [10] are some amorphous systems where this theoretical notion [5] was experimentally validated.

Thermoelectric devices often operate under harsh working conditions, being exposed to cyclic heating and atmosphere [1,2]. They can also include exposure to combustion flames [1,2]. However, these secondary features are often overlooked in design efforts. It is known that commercial thermoelectrics can readily oxidize at 500 K [11], but many physical mechanisms have only recently been investigated. For instance, Bi₂Te₃, a well-explored thermoelectric compound, oxidizes in a poly-crystalline form, but the Te-terminated basal planes are inert [12,13].

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Furthermore, oxidation of TiNiSn is characterized by inertness of Ni [14,15], which is counterintuitive since Ni forms oxides.

Thermal shock occurs when a system, such as a thermoelectric device, is subjected to abrupt temperature variations yielding enormous heat and stress gradients, which may result in mechanical damage and structural failure [16]. Physical properties governing the thermal shock response are also relevant for other thermomechanical properties, such as thermal fatigue [17]. The thermal shock resistance is usually described by the thermal shock parameter \( R_T \):\(^{(1)}\)

\[
R_T = \sigma_f(1 - \nu) a Y
\]

where \( \sigma_f, \nu, a, \) and \( Y \) are flexural strength (proportional to tensile strength), Poisson’s ratio, linear coefficient of thermal expansion, and elastic (Young’s) modulus, respectively [16,18]. All these thermomechanical properties are seldomly taken into account in a single study (the same level of approximations or the same sample for analyses) [18,19]. An equivalent parameter for the thermal fatigue behavior contains yield strength instead of flexural strength [17]. To enhance the thermal shock resistance, \( R_T \) should be maximized, which is a challenging task. High \( \sigma_f \) gives rise to crack tip blunting or crack deflection, high \( k \) takes heat away from an active zone and diminishes the temperature gradients, a large \( \nu \) value is usually connected with a ductile fracture rather than brittle so that fewer cracks are initiated, as well as a product of low \( a \) and small \( Y \) fosters low thermal stresses [16,18]. Some authors have claimed that thinner samples are less prone to thermal shock [20], but this is not captured in Eq. (1). It seems that a contradiction occurs with the enhancement of \( ZT \) for thermoelectric devices. Namely, a high \( k \) value is preferred for a high \( R_T \), but a low \( \nu \) value is desired for a high \( ZT \). However, it is not clear how other properties of an amorphous solid contribute to \( R_T \) and how they are interconnected.

There are no modelling attempts to describe amorphous (thermoelectric) solids in terms of \( R_T \), extending the notion introduced by Nolas and Goldsmid [5] to the secondary properties. Ignoring such secondary features (thermal shock or fatigue and oxidation) in design efforts of novel thermoelectric devices for green energy generation may lead to failure.

Cubic half-Heusler phases (space group F-43m) are selected as a benchmark thermoelectric system. These ternary compounds have been known for a very long time [21]. An example is ZrNiSn, where Zr and Sn span a NaCl matrix, while Ni forms a zinblende sublattice with Sn atoms [22–25]. 50 % of the Ni sublattice is occupied [26,27]. Ti or Hf often replace Zr in such compounds, while Sb can substitute Sn [26,27]. In general, the half-Heusler phases possess exciting properties, including superior mechanical properties (high elastic modulus and hardness) to many other thermoelectric systems, approaching those of Al2O3 [28,29], which is a well-known hard oxide used for abrasive and refractory applications. Furthermore, the half-Heusler compounds are known to be stable and non-toxic [26,27]. The maximum \( ZT \) value of the half-Heusler phases is close to 1.5, with a potential for further enhancements [26]. In particular, ZrNiSn in its intrinsic form reaches a \( ZT \) value of about 1.0 [24], but it can approach 1.5 when alloyed with Ti and Hf [30]. It may exhibit some characteristics of a disordered alloy due to the presence of Ni at the interstitial sites [31], which is relevant for scattering of electrons and phonons. ZrNiSn [32] oxidizes in a similar fashion as TiNiSn [14,15], as discussed above, but its oxides are less thick, indicating a higher level of inertness. It appears that ZrNiSn is the only half-Heusler phase considered so far in the amorphous state [6]. It has been reported that such a state yields a low \( \nu \) value of 1.4 W m\(^{-1}\) K\(^{-1}\) at room temperature [6], which is beneficial for thermoelectric applications. Still, no thermomechanical properties have been explored for amorphous ZrNiSn.

In this work, density functional theory (DFT) [33] and two acoustic phonon models (Slack [34,35] and Debye-Grueneisen [36]) are synergistically employed to obtain \( R_T \) for crystalline and amorphous half-Heusler ZrNiSn. Owing to complex mechanical loading during flexural strength measurements (three-point bending) [37], \( \sigma_f \) is not considered in this DFT study. The other four parameters, \( \kappa, \nu, a, \) and \( Y \), constituting \( R_T \) (see Eq. (1)) are explored for crystalline and amorphous ZrNiSn. Thus, the thermal shock behavior is described by DFT and the applied phonon models as \( R_T / \sigma_f \) and referred to as an intrinsic thermal shock parameter. Our ambition is to critically appraise the applicability of the notion by Nolas and Goldsmid [5] on the secondary properties of thermoelectric compounds. Furthermore, the origin of the thermomechanical response of crystalline and amorphous ZrNiSn is unraveled by analyzing the electronic structure.

2. Theoretical methods and models

To obtain \( R_T / \sigma_f \) for crystalline and amorphous ZrNiSn, two DFT codes were employed. While DFT modelling of a crystalline configuration is straightforward (12 atoms in the unit cell of crystalline ZrNiSn), describing an amorphous state is more challenging. Here, the so-called liquid-quench algorithm was used [38]. First, a large supercell (324 atoms) was created based on the crystalline ZrNiSn unit cell, which was then heated to 2500 K, well above the melting point. Second, the supercell was quenched to 0 K, the interatomic forces were minimized, and the equilibrium volume was calculated. To enable the high computational speed needed for the description of the amorphous state, the OpenMX code was used [39]. A linear combination of localized pseudopotentials [40] and the generalized-gradient approximation (parametrization by Perdew, Burke, and Ernzerhof [41]) were employed. The following basis set was considered: Zr7.0–s3p2d2, Ni6.0s–s3p3d2f1, and Sn7.0–s2p2d3f1, where the chemical symbol is followed by the cut-off radius in the Bohr atomic units and the used orbitals (not to be confused with the electronic configurations).

An energy cut-off of 150 Ry (2041 eV) was selected to obtain the total energy precision of 10\(^{-6}\) Ry (13.6 meV) within a real-space grid of 45x45x45 for the ZrNiSn unit cell. Spin polarization was not considered. DFT-based molecular dynamics simulations were carried out to melt and quench the supercell of ZrNiSn (velocity scaling thermostat, canonical ensemble). The molten state was equilibrated for 1000 fs.

Using the amorphous ZrNiSn configuration from the OpenMX code, the Vienna \textit{ab initio} simulation package (VASP) was applied for further calculations at 0 K. The OpenMX code is faster, but the VASP code has a higher precision [42]. All exchange-correlation approximations were made on the same level. The projector-augmented plane-wave potentials [43–45] were considered in the VASP code instead of pseudopotential orbitals. Full structural optimization was carried out by minimizing the interatomic forces and obtaining the equilibrium volume at 0 K. The convergence criterion for the total energy was 0.01 meV per atom and a 500 eV cut-off was employed. The integration in the Brillouin zone was carried out on a converged Monkhorst-Pack 4x4x4 k-point mesh [46] for the amorphous configuration and 12x12x12 for crystalline ZrNiSn. The convergence tests were carried out for the total energy and elastic constants. Increasing the number of k-points in all directions by 50 % and 100 %, the total energy was within 0.01 meV per atom and the elastic constants were within 0.7 GPa. The electronic structure was explored by analyzing the density of states.

With the input from DFT, two acoustic phonon models were used in the present work to describe the thermomechanical behavior of crystalline as well as amorphous half-Heusler ZrNiSn and calculate \( R_T / \sigma_f \), a relevant secondary property for thermoelectric devices. The values for \( \kappa, \nu, a, \) and \( Y \), constituting \( R_T / \sigma_f \) (see Eq. (1)), were thus calculated. Considering the Umklapp phonon–phonon scattering in the Slack model [34,35], \( \kappa \) values were calculated as \( \kappa = A \frac{MD^2 \delta \nu^{1/3}}{r^2 F} \)

where the factor \( A \) is the following constant.

\[ <important> \text{Computational Materials Science 230 (2023) 112530} \]</important>
\[ A = \frac{2.43 \times 10^{-6}}{1 - 0.514 \gamma^{-1} + 0.228 \gamma^{-2}} \]  

(3)
determined by \( \gamma \), which is the Grüneisen parameter \([47,48]\). \( M \) is the average atomic mass and \( D_0 \) is the Debye temperature for acoustic phonon modes. In addition, \( \delta^3 \) and \( n \) in Eq. (2) are the volume per atom and the number of atoms, respectively \([34]\). The values for \( \gamma \) and \( D_0 \) were estimated from elastic constants \([47,49]\). All cubic elastic constants, \( C_{11} \), \( C_{12} \), and \( C_{44} \), were obtained using a computational approach described elsewhere \([50]\). The cubic symmetry was maintained for the amorphous configuration. The elastic constants were also used to acquire \( c \) and \( Y \) for ZrNiSn within the Hill approximation \([51]\), assuming a polycrystalline aggregate.

The Debye–Grüneisen model was applied to estimate the \( a \) values \([36]\) of ZrNiSn. Within this model, the Helmholtz free energy \( F \) can be specified as

\[ F = E - n_k T \left[ 3 \left( \frac{T}{D} \right)^{\frac{3}{2}} \int_0^{D} \frac{x^3}{e^x - 1} dx - 3 \ln \left( 1 - e^{-\frac{3}{2}} \right) \right] \frac{9D}{8T} \]  

(4)

with \( E \) and \( k_B \) being the total energy and the Boltzmann constant, respectively. These data were fitted to the Birch-Murnaghan equation of state \([52]\) to calculate the equilibrium volume and bulk modulus of the ZrNiSn configurations as a function of \( T \). The bulk moduli were further employed to estimate the temperature-dependent \( Y \) and \( a \) was calculated from the temperature-dependent equilibrium volume.

To estimate the thermoelectric \( ZT \) value (primary properties) at room temperature (300 K), the following procedure was employed. The Seebeck coefficient \( (S) \) was estimated from the density of states \( (D) \) within the semiclassical Boltzmann transport theory under the assumption of a constant relaxation time \( (\tau) \):

\[ S = \frac{k_B}{q} \int_{-\infty}^{+\infty} \frac{\partial f_{FD}}{\partial E} D(E) \frac{\tau}{\tau_E} dE \]  

(5)

where \( f_{FD} \), \( q \), and \( E_F \) designate the Fermi-Dirac distribution, unit charge, and Fermi energy, respectively \([53]\). The band velocity \( (v) \) was assumed to be the Fermi velocity and hence constant. For the density of states calculations, 1201 grid points (energy divisions) were considered, and the frozen band approximation was assumed. Furthermore, using the Boltzmann transport theory \([53]\) the electrical conductivity \( (\sigma) \) was obtained:

\[ \sigma = -q^2 \int_{-\infty}^{+\infty} \frac{\partial f_{FD}}{\partial E} D(E) v^2 \tau dE \]  

(6)

All amorphous configurations were obtained by the OpenMX code, which served as input for VASP. The VASP code was only used to obtain the total energies and density of states at 0K, while all physical properties were calculated by numerically solving the corresponding equations.

3. Results and discussion

The calculated lattice parameter of crystalline ZrNiSn at 0 K is 6.182 Å, which deviates by 1 % from the experimental value (6.109 Å) \([54]\). This is an acceptable agreement for the exchange–correlation functional employed in the current study \([55]\). The generalized-gradient approximation usually overestimates the lattice parameters \([55]\), which is also the case herein. The unit cell of crystalline ZrNiSn is provided in Fig. 1 together with the amorphous configuration obtained in this work by the liquid-quenching algorithm \([38]\). The nearest neighbor distance in the crystalline counterpart is 2.677 Å both for Zr–Ni and Sn–Ni. In the amorphous state, the nearest neighbor distance is no longer discrete but peaks at the same interatomic distance. The crystalline and amorphous configurations in Fig. 1 can readily be compared via mass density, reaching 7.553 and 7.332 g cm\(^{-3}\), respectively. Clearly, the density is lower for the amorphous state due to a decreased coordination and a lack of long-range order. This may affect the physical properties.

The calculated thermal conductivity \( (\kappa) \) data for crystalline and amorphous ZrNiSn as a function of temperature are provided in Fig. 2. It is the first out of four parameters, \( \kappa, v, a, \) and \( Y \), constituting \( R_T / \sigma_T \) (see Eq. (1)), which is addressed herein. At room temperature (300 K), a deviation between the calculated value for the crystalline state of 5.6 W m\(^{-1}\) K\(^{-1}\) \([56]\) and the measured data is 5 %. Even better agreement is achieved for the amorphous state (the deviation is essentially 0 %) \([6]\). The difference between the crystalline and amorphous state is fourfold. This agrees with the notion of Nolas and Goldsmid \([5]\). Clearly, a lack of long-range order gives rise to phonon–phonon scattering and a low \( \kappa \) value. This should be beneficial for thermoelectric devices as the \( ZT \) parameter should drastically increase. This is consistent with the literature \([6]\). As the temperature increases, the \( \kappa \) values for both crystalline and amorphous ZrNiSn decrease (see Fig. 2). The data for the amorphous state are consistent with the amorphous limit \([57,58]\). There are no experimental data for amorphous ZrNiSn to compare with. The data for crystalline ZrNiSn \([56]\) exhibit the same trend, but the slopes for the calculated data are higher. It is not straightforward to identify the origin of this deviation. Still, it can be speculated that this may be due to the applied approximations as well as possible defects and residual stress in

![Fig. 1. Structure of crystalline (left panel) and amorphous ZrNiSn (right panel). Zr atoms are green, Ni atom light gray, and Sn atoms dark gray.](image-url)
It is indisputable that the amorphous state exhibits a four-fold reduced $\kappa$ value, thereby drastically increasing $ZT$.

The calculated thermal expansion data ($\alpha$) for amorphous and crystalline ZrNiSn are given in Fig. 3. Both data sets show an increase with temperature and a saturation above room temperature. This behavior is consistent with the general trends reported in the literature on other systems, such as crystalline Cu [60], CuInSe$_2$ [61], and Si [62] as well as Pd-Al-Y-Ni metallic glass [63]. The literature data on the linear coefficient of thermal expansion for crystalline ZrNiSn are only available in an averaged form for the temperature range of 200 to 800 K [28], as indicated in Fig. 3. A deviation between the calculated and measured data [28] at 300 K for crystalline ZrNiSn is from 2 % to 6 %. Using the Debye-Grüneisen model [36] on 20 crystalline thermoelectric systems, the deviation between the theoretical and experimental data for $\alpha$ seems to be within 30 % [64]. Hence, the data in this work are in good agreement with the available experimental values [28]. Our data on crystalline ZrNiSn are also consistent with the theoretical predictions based on the quasi-harmonic approximation [65]. It is important to note that the linear coefficient of thermal expansion is 19 % to 32 % higher for the amorphous state in the explored temperature window. Obviously, the effect of the loss of long-range order on $\alpha$ (Fig. 3) is not as high as on $\kappa$ (Fig. 2).

Finally, the mechanical properties of ZrNiSn are discussed. The calculated elastic constants at 0 K are: $C_{11} = 191$ GPa, $C_{12} = 80$ GPa, and $C_{44} = 54$ GPa for crystalline ZrNiSn as well as $C_{11} = 167$ GPa, $C_{12} = 74$ GPa, and $C_{44} = 43$ GPa for amorphous ZrNiSn. The calculated Poisson ratio for crystalline and amorphous ZrNiSn at 0 K is 0.298 and 0.315, respectively, as obtained from the elastic constants. The reported experimental data for crystalline ZrNiSn are: $\nu = 0.271$, $C_{11} = 215$ GPa, and $C_{44} = 67$ GPa [28]. Thus, the deviation between the calculated and measured data obtained by resonant ultrasound spectroscopy is within 9 %, 13 %, and 19 % for these three parameters, respectively. This is an acceptable agreement for the selected exchange–correlation functional employed in this work [55]. The calculated elastic (Young’s) modulus data for crystalline and amorphous ZrNiSn as a function of temperature are provided in Fig. 4. The elastic modulus for both crystalline and amorphous ZrNiSn slowly decreases with temperature, being consistent with the literature [28]. However, there are deviations considering the absolute scale. At room temperature (300 K), the calculated elastic modulus deviates by 24 % from the measured value obtained by resonant ultrasound spectroscopy [28], 1 % from the experimental value extracted by nanoindentation [66], 1 % from the measured value by ultrasonic characterization [67], and 23 % from the classical molecular dynamics data (embedded atomic model) [68]. As the calculated elasticity data are expected to be within 20 % from the experimental values based on the selected exchange–correlation functional [55], an attempt is made to explain the deviations. The experimental samples are polycrystalline [28,66,67], and they may contain defects as well as may be under stress. Residual stress readily affects the elastic properties [69,70]. Hence, compressive stresses are assumed in our model and the elastic modulus data at $-2$ and $-4$ GPa are also provided in Fig. 4. While such high compressive stresses may appear high for bulk materials, they are readily available in thin films [71]. At $-2$ GPa and 300 K, the...
deviation between the calculated and measured value [28] is 18%, and it further decreases to 12% at -4 GPa and 300 K. This indicates that residual stresses may be present in the sample evaluated previously [28]. In any case, the amorphous state of ZrNiSn exhibits a lower elastic modulus than the crystalline counterpart in the whole temperature range (Fig. 4), but the drop is as not as pronounced as for $\kappa$ (Fig. 2). Still, a smaller elastic modulus is beneficial for resistance against thermal shock (see Eq. (1)).

Taking all the data on ZrNiSn into account (Fig. 2, Fig. 3, and Fig. 4), the intrinsic thermal shock parameter ($R_T/\sigma_f$) can be obtained employing Eq. (1), and the results are plotted in Fig. 5. The intrinsic thermal shock parameter decreases as a function of temperature, whereby the crystalline state is by a factor 4 higher than the amorphous one in the probed temperature range. This is precisely the same relationship obtained for $\kappa$ (Fig. 2). It seems that the intrinsic thermal shock parameter is dominated by $\kappa$ rather than the other parameters in Eq. (1) when amorphous and crystalline states are compared. As there are no available data on the intrinsic thermal shock parameter for ZrNiSn, a comparison is made with other systems of interest (see Fig. 5). Crystalline Gd$_3$Sc$_2$Ga$_3$O$_{12}$ and LiF [18] can be used as high-power lasers, implying enormous thermal loads and thus a need for a high thermal shock resistance parameter. Clearly, crystalline ZrNiSn would perform well since it exhibits a similar value of the intrinsic thermal shock parameter. However, it is not a priori clear if the intrinsic thermal shock parameter for amorphous ZrNiSn is high enough to withstand high thermal loads during operation. It has been reported that hydrogenated amorphous carbon samples perform well under thermal shock [72], but no thermal shock parameter data are available. More studies are needed for the thermal shock behavior of amorphous systems.

It remains to identify the physical origin of the difference in the thermomechanical response between crystalline and amorphous ZrNiSn. Obtaining a physical picture, rather than only providing a quantitative description of $R_T/\sigma_f$ (thermomechanical response), is of importance. Hence, the data for the total density of states for these two configurations are provided in Fig. 6. There are two distinctive energy regions: (i) a discrete region at about ~7 eV and (ii) a broad and continuous region from ~5 eV and above the Fermi level. The data for the crystalline state are consistent with the literature [73,74]. The crystalline state shifts towards lower energies, which implies that the bonding strength is higher than that of the amorphous state.

Crystalline ZrNiSn is further analyzed in terms of its electronic structure by exploring the partial density of states provided in Fig. 7. Zr 3d and Ni 3d states overlap in the range from ~5 eV to the Fermi energy. Likewise, Sn 5p and Ni 3d states overlap in the same energy range. This is indicative of a covalent interaction. Sn 5s states dominate the energy bands at about ~7 eV. As Zr and Sn are not the nearest neighbors, the orbital overlap between them is minute. Due to the presence of the d states in the vicinity and at the Fermi level from both Zr and Ni, some metallic contribution to the overall bonding is possible. This is consistent with the literature [73]. It can be deduced based on the comparison between Fig. 6 and Fig. 7 that the stronger bonding in the crystalline counterpart is likely due to an enhancement of the Zr 3d – Ni 3d and Sn 5p – Ni 3d hybridization (the shift to the lower energies in Fig. 6) and a higher coordination (the amorphous state is characterized by a lack of long-range order and thus a lower coordination). This can be used to explain the thermomechanical data discussed above. Stronger bonds in the crystalline state imply lower thermal expansion (Fig. 3) and higher
4. Conclusions

As stated above, thermal conductivity affects the intrinsic thermal shock parameter more than any other parameters in Eq. (1) when a comparison between amorphous and crystalline states is considered. There is a fourfold decrease for the amorphous state of ZrNiSn (see Fig. 2). Based on the definition of $ZT$, as provided above, and the notion of Nolas and Goldsmid [5], this is desired. However, it constitutes a conflicting requirement for the optimum performance of thermoelectric devices considering both primary and secondary properties since a high resistance to thermal shock or fatigue is favored by a high $\kappa$ value. It remains to be seen experimentally if somewhat lower values of the intrinsic thermal shock parameter for amorphous ZrNiSn suffice for high-temperature applications. One can speculate how to circumvent this apparent conflict. Instead of fully amorphous samples, one could consider samples with nanosized grains embedded in an amorphous matrix. This could give rise to a high level of phonon-phonon scattering to meet the requirements for high thermoelectric efficiency (intermediate $\kappa$ and hence high $ZT$) as well as considerably high $R_T$ (intermediate $\mu$). For instance, overstoichiometric samples in Sn or Ti, rather than Ni since its sublattice is only 50% occupied, may give rise to an amorphous tissue phase surrounding ZrNiSn grains, equivalent to Fe in amorphous Fe-Pt-Ir-O [75], TiB$_2$ in ultra-thin amorphous B [76], or TiN in amorphous Si-N [77]. Similarly, multilayered samples (amorphous/crystal lines) may yield comparable results. Clearly, more systematic work is needed to tackle the thermomechanical response of thermoelectric devices. It also remains to be seen how the oxidation resistance of ZrNiSn is affected by crystallinity or a lack thereof. Amorphous systems may inhibit oxidation due to an absence of grain boundaries, but this also specific for each system so thorough investigations are indispensable.

The scope of this work is to address the secondary (thermoelectric) properties of ZrNiSn, but some discussions on the primary (thermoelectric) properties can be valuable. The calculated Seebeck coefficient for crystalline and amorphous ZrNiSn at 300 K is $-32$ and $-3 \mu V K^{-1}$, respectively. The data for the crystalline counterpart are consistent with the values measured on samples synthesized by arc melting ($-20 \mu V K^{-1}$) [78] and laser melting ($-60 \mu V K^{-1}$) [79]. However, the most of reported values at 300 K are in the range of $-150 \mu V K^{-1}$ [67]. Such deviations may be due to the applied approximations, but also due to sensitivity of the Seebeck coefficient to the band gap size [81], which is not of relevance for the secondary properties, and defects, including the intrinsic ones [73]. A decrease of the absolute value of the Seebeck coefficient for the amorphous state is consistent with the data on isostructural TiNiSn [82]. This may be counterbalanced by doping or alloying, as demonstrated for amorphous NbO$_2$ [83]. Since the relaxation time is required to obtain the absolute value of the electrical conductivity (see Eq. (5)), only the ratio between the crystalline and amorphous state of ZrNiSn is roughly estimated to be 17. Thus, the thermoelectric figure of merit $ZT$ seems to be lower for the amorphous state of ZrNiSn, but it is very likely that this can be compensated by doping or alloying.

4. Conclusions

Ternary half-Heusler ZrNiSn has been considered for thermoelectric applications in terms of its thermomechanical properties. Amorphous ZrNiSn exhibits a fourfold lower thermal conductivity than the crystalline counterpart, which is beneficial for thermoelectric performance. However, this is a conflicting requirement to obtain a pronounced thermal shock or thermal fatigue resistance. Owing to stronger bonding in the crystalline counterpart mediated through an enhancement of the $Zr$ 3d – $Ni$ 3d and $Sn$ 5p – $Ni$ 3d hybridization and higher coordination, its linear coefficient of thermal expansion is lower, and the elastic modulus is higher than in the amorphous state. Together with lower acoustic phonon–phonon scattering, the crystalline state of ZrNiSn possesses the higher intrinsic thermal shock parameter, rather close to materials used as high-power lasers. It should be noted that the smaller elastic modulus of the amorphous state is beneficial for resistance against thermal shock, giving rise to low thermal stresses. Experiments are required to appraise if the amorphous state of ZrNiSn can bear high thermal loads during operation. It is speculated that samples with amorphous and crystalline regions may satisfy the requirements for high $ZT$ and high $R_T$. This work is expected to inspire more experimental work on amorphous thermoelectric compounds considering both primary and secondary properties in a holistic manner.

CRediT authorship contribution statement

Denis Music: Conceptualization, Methodology, Data curation, Writing – original draft, Visualization, Investigation, Project administration, Funding acquisition. Sana Khayyamifar: Investigation, Writing – original draft. Johan Hektor: Conceptualization, Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References


