Dual-Substitution in Ti($Fe_{0.5}Ni_{0.5}$)Sb Half-Heuslers for Thermoelectric Performance Optimization

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Abstract:

Ti($Fe_{0.5}Ni_{0.5}$)Sb is a prospective candidate for next-generation thermoelectric devices, but its application is limited by poor thermoelectric performance. It's found that dual substitution of Hf and Fe in Ti($Fe_{0.5}Ni_{0.5}$)Sb can achieve a zT of 0.51 around 850 K, potentially increasing at higher temperatures, by suppressing phonon transport and increasing carrier concentration. Fe doping also shifts the onset of bipolar conduction toward higher temperatures, mitigating a source of performance breakdown. This work realizes the pathway to high-performance, high-temperature thermoelectric materials based on Ti($Fe_{0.5}Ni_{0.5}$)Sb.

Summary of Research:

Half-Heusler thermoelectric-based devices are candidates to combat the growing global energy demand by harvesting waste heat. The performance of thermoelectric materials is evaluated by the unitless Figure of Merit $zT = S^2GT/K$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and K is the thermal conductivity (summation of lattice component (KL) and electronic component (Ke), representing contributions from phonons and carriers, respectively). Enhanced phonon suppression from the increased structural complexity in Ti($Fe_{0.5}Ni_{0.5}$)Sb can reduce the performance-limiting KL in half-Heuslers [1]. Additionally, high-temperature annealing or the presence of Hf induces p-type behavior via Sb vacancy formation, useful for device applications [2]. However, pristine Ti($Fe_{0.5}Ni_{0.5}$)Sb can only achieve a zT around 0.03 below 800 K [2]. Considering the interconnected nature of S, σ, and K, improving this value is effectively done by decreasing KL and increasing the power factor (S2σ). The former can be achieved by substituting heavy atoms like Hf at the Ti site, disrupting phonon transport, and the latter by modifying the Fe/Ni ratio to favor Fe, increasing carrier concentration.

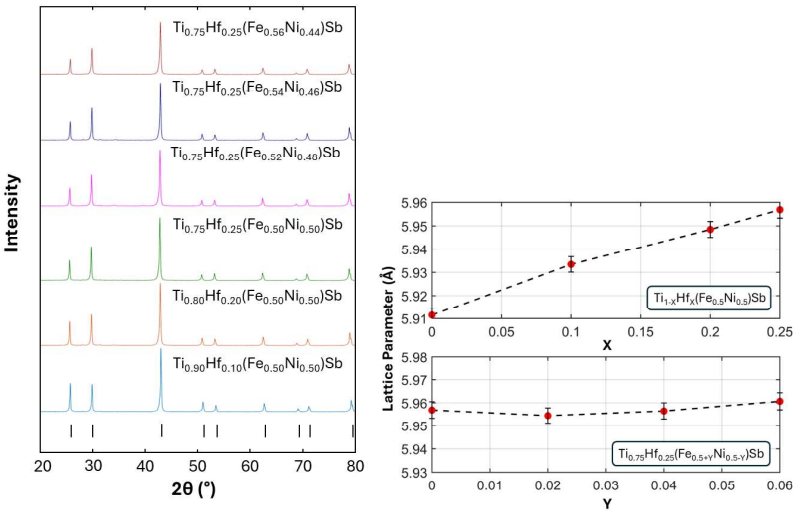

Figure 1: XRD Intensity vs 20 of all samples with relevent peaks for undoped quaternary-Huesler spectra denoted by black vertical lines (left) and lattice parameter vs Hf and Fe doping concentrations (right).

To evaluate the impact of dual substitution of Hf and Fe on S, σ, K, and zT in Ti($Fe_{0.5}Ni_{0.5}$)Sb, Ti (mixed with Ni, Fe and/or Hf) and $FeSb_2$ were first prepared via arc melting and solid-state synthesis, respectively. Both were then ball milled and underwent Spark Plasma Sintering. Phase composition of the final alloy was determined by XRD (X-ray diffraction), while S and σ were quantified via thermally coupled 4-probe measurements. Thermal conductivity was determined by Laser Flash Analysis, where K_e was extracted via the Wiedemann-Franz Law ($K_e = L\sigma T$), where L is the Lorentz number.

Figure 1 shows the XRD spectra and lattice parameter of samples doped with Fe and/or Hf. All six spectra align with the peak positions for the quaternary Heusler phase, indicating no significant secondary phase formation. Additionally, all peak positions in the six samples are shifted to a lower 2θ, indicating expansion of the lattice. This is reflected in the increased lattice parameter resulting from Hf, a larger atom than Ti, substitution, emphasizing that little

to no performance-inhibiting dopant segregation is present. The amount of lattice expansion expected with Fe doping is indiscernible from measurement error.

The impact of Hf and Fe doping on K, σ, S, and zT from 300K to 850K is shown in Figure 2. An observed 2x or greater reduction in thermal conductivity (compared to pristine $Ti(Fe_{0.5}Ni_{0.5})Sb$ prepared under similar conditions [2]) and its inverse relationship with Hf doping is indicative of increased phonon scattering, diminishing KL. While Fe doping does increase carrier concentration and Ke, negatively impacting performance, Ke still has minimal impact at 852 K with 6% Fe substitution, where this effect is the most dominant.

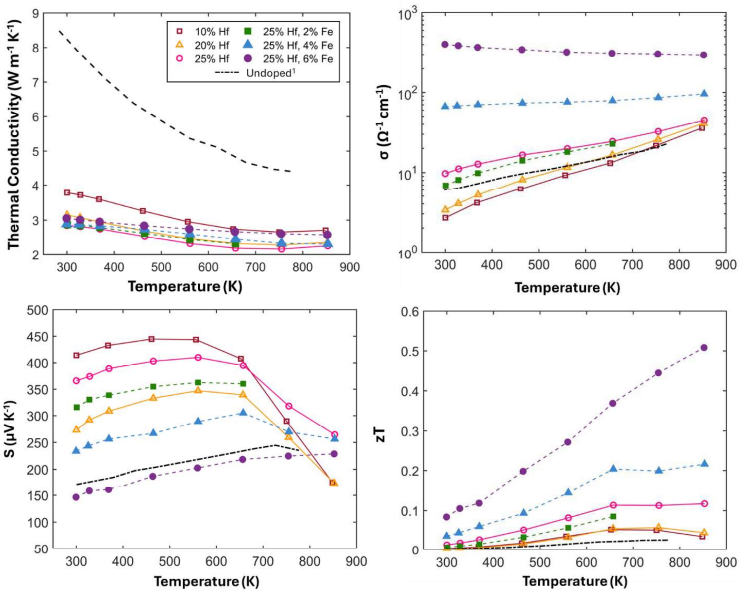

Figure 2: Thermal Conductivity (Wm-1K-1), Electrical Conductivity (Ω-1cm-1), Seebeck Coefficient (μV K-1) and Figure of Merit vs Temperature (K) for all samples and undoped reference sample.

The performance impact of Fe substitution increasing K_e is outweighed by a larger increase in electrical conductivity. With 6% Fe doping, metallic behavior is observed in the electrical conductivity plot, emphasizing the dramatic impact Fe substitution has on electrical transport. There is also a slight increase in electrical conductivity with Hf doping from the additional loss of Sb during synthesis. As corroborated by the positive Seebeck coefficients observed in all samples, 10% Hf doping increases Sb loss enough to induce p-type behavior without additional high-temperature annealing.

Reductions in S shows direct proportionality with Hf and Fe doping, where inconsistencies in this pattern attributed to sample quality or measurement error cannot be confirmed without reiterative testing. Almost all samples show a stark decrease in S at higher temperatures from the onset of bipolar conduction. This is delayed to higher temperatures with 6% Fe doping due to the Fermi level shift towards the valence band. Therefore, more thermal energy is necessary to shift the Fermi level back towards the center of the bandgap to trigger the onset of bipolar conductivity.

The highest concentrations of Hf and Fe substitutions tested lead to an 18x increase in zT at ~750K compared to undoped $Ti(Fe_{0.5}Ni_{0.5})Sb$. Dual substitution shows a more profound impact on zT compared to Hf doping alone, from the significant impact that Fe doping has on electrical conductivity. Notably, the consistent increase in zT for the 6% Fe-doped sample beyond 650K is due to the delay in the onset of bipolar conductivity, where preserving performance at higher temperatures leads to a zT of 0.51 at 852 K.

Conclusion and Future Steps:

The results of this work have found that dual substitution of Hf and Fe increase the zT of $Ti(Fe_{0.5}Ni_{0.5})Sb$ by decreasing KL and increasing σ, while also delaying the onset of bipolar conduction to higher temperatures. Observing the bipolar effect in all samples can be accomplished in future work by conducting a similar analysis at higher temperatures. This is to be coupled with additional high-temperature annealing, to understand how further Sb loss impacts the thermoelectrical performance of doped $Ti(Fe_{0.5}Ni_{0.5})Sb$.

References:

[1] S. Anand et al., "Double Half-Heuslers," Joule, vol. 3, no. 5, pp. 1226–1238, May 2019, doi: 10.1016/j.joule.2019.04.003.

[2] I. Serhiienko et al., "Pivotal role of Sb vacancies in quaternary half-Heusler thermoelectrics," J. Mater. Chem. A, vol. 13, no. 20, pp. 15268–15277, May 2025, doi: 10.1039/D5TA01437A.