4-27-2018

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Introduction and Background

- Thermoelectric (TE) devices convert heat absorbed into electricity with no moving parts
- Reliable, zero-maintenance, scalable operation up to 1300K
- TE devices are needed in nuclear industry for harvesting heat to power wireless sensors
- Half-Heusler alloys are semiconductors with modest conversion efficiency
- State-of-the-Art devices use Hafnium (10X $ of Zirconium); investigated a Ti/Zr alternative

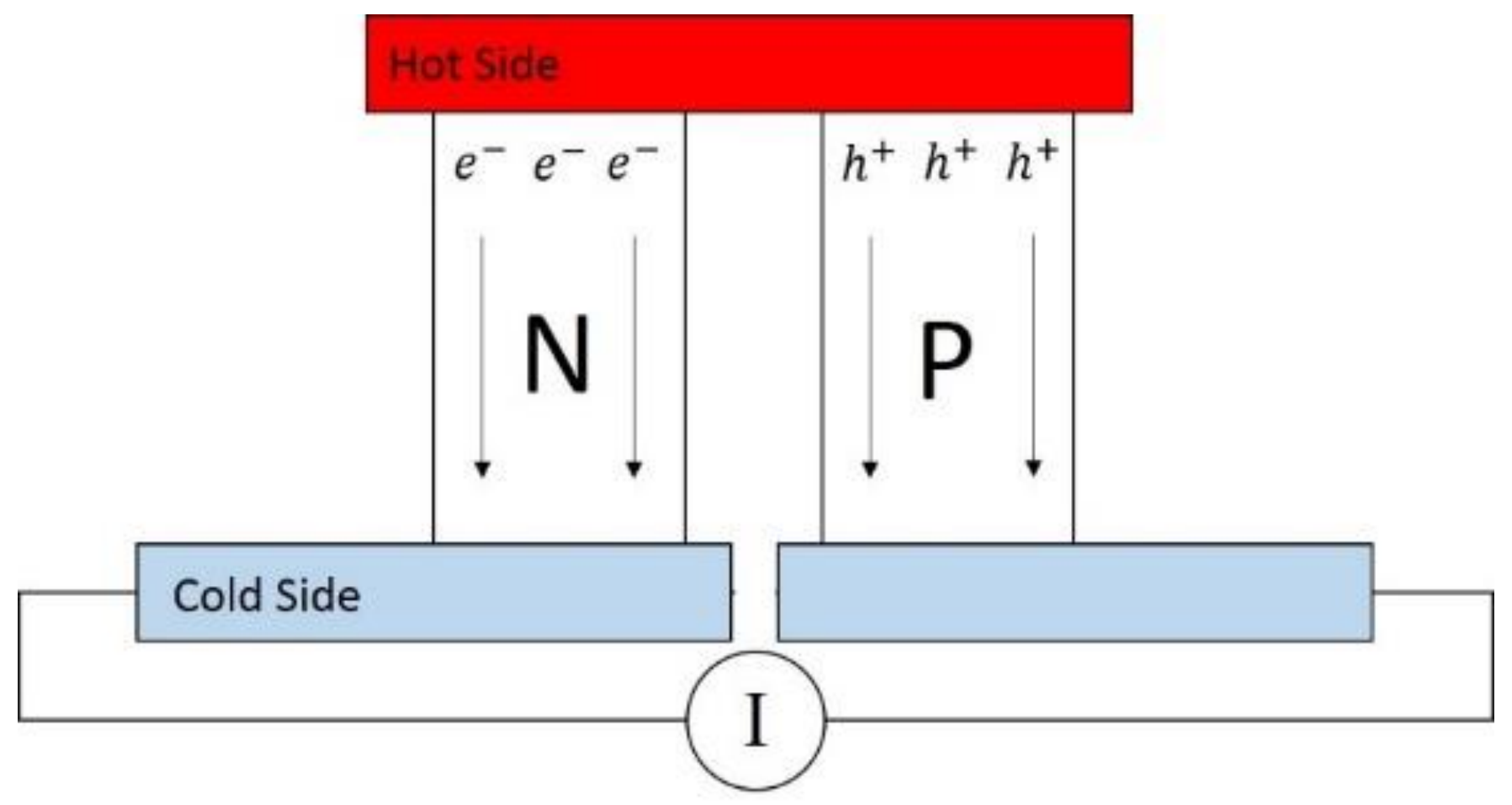


Figure 1. Thermoelectric device operating principle

The ZT is the performance figure of merit; a higher ZT indicates higher conversion efficiency

$$ZT = \frac{S^2\sigma}{K_{(e+l)}}T = \frac{S^2}{a\rho_M\rho_R C_p}T$$

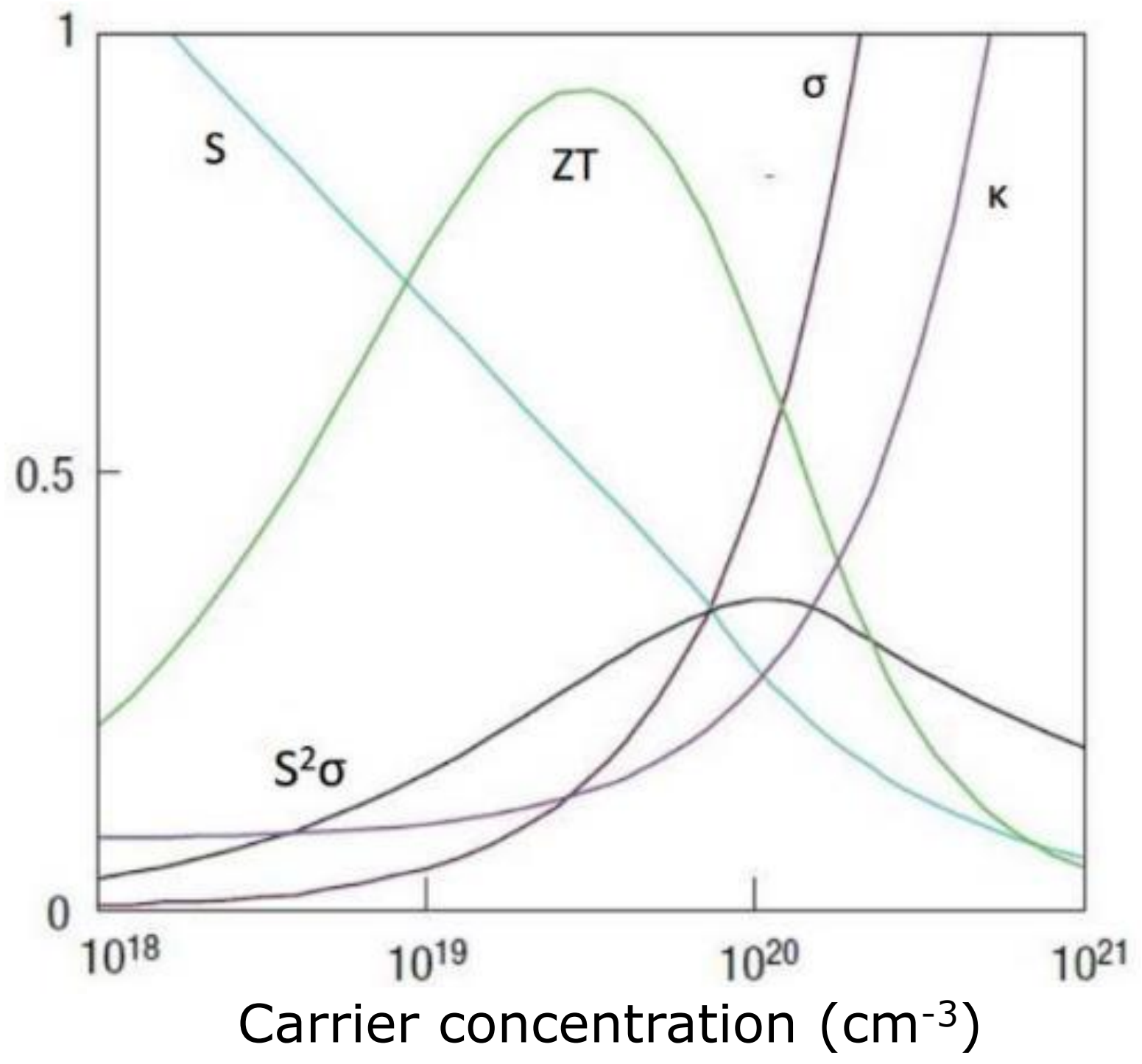


Figure 2. ZT parameter interdependency on carrier concentration[1]

S: Seebeck coefficient ($^V/_K$)
σ: electrical conductivity ($^S/_m$)
k: thermal conductivity ($^W/_{mK}$)
T: absolute temperature (K)
ρ_R: electrical resistivity (Ωm)
ρ_M: mass density ($^g/cm^3$)
α: thermal diffusivity (m^2/s)
C_p: Specific heat capacity ($^J/_{kgK}$)

Heat capacity given by Kopp–Neumann law:

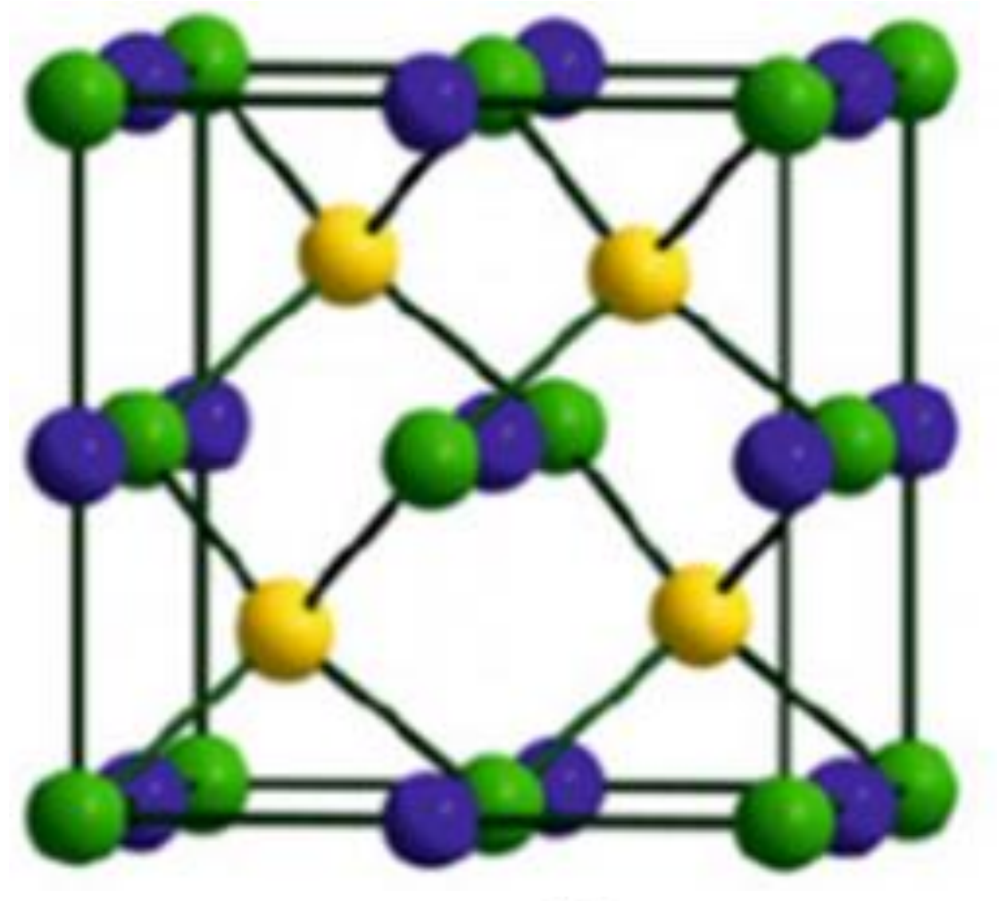
$$C_p = \sum C_i f_i$$

C_i: elemental heat capacity
f_i: mass fraction

Half-Heusler Thermoelectric Materials

Half-Heusler
- XYZ 1:1:1 stoichiometry
- 4/8 vacant 4c sites
- 18 valence electrons gives semiconductor behavior
- Ionic rock salt & covalent zinc blende bonding

Full-Heusler
- XY_2Z 1:2:1 stoichiometry
- No vacant 4c sites



	N-type	P-type
● 4a	Nb/Ti/Zr/Hf	Nb/Ti
● 4b	Sn/Sb	Sb
● 4c	Ni	Fe

Figure 3: Half-heusler unit cell
Space group: F4/3m, No. 216
Wycoff positions[2]:
4a (0,0,0) 4b (½ ½ ½) 4c (¼ ¼ ¼)

Advantages
- Intermediate service temperatures (700K)[2]
- Intermediate performance ZT≈1-1.5 [2]
- XYZ site compositional tailoring ↑ ZT
- High power factor (numerator of ZT)
- Abundant raw materials (except Hafnium)
- Low toxicity raw materials

Disadvantages
- High intrinsic thermal conductivity
- Brittle

Can reduce thermal conductivity by grain size reduction & mass disorder effects

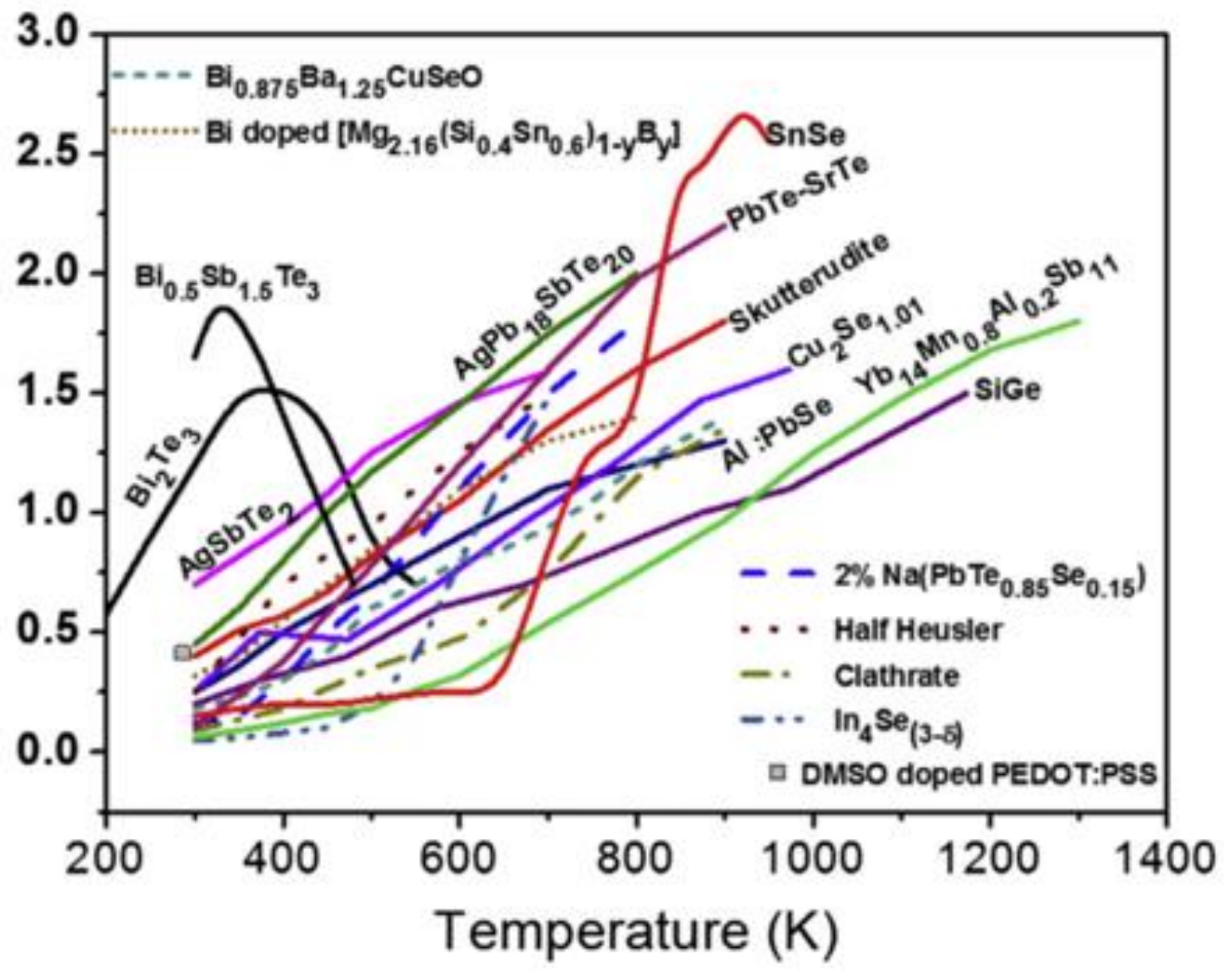


Figure 4. ZT of half-heuslers relative to other TE materials and applicable service temperatures[1]

Synthesis Route for Half-Heusler: $Ti_{0.75}Zr_{0.25}NiSn_{0.98}Sb_{0.02}$

- Mechanical alloying (MA) via ball milling uses repeated weld/fracture events to alloy powder
- Spark plasma sintering (SPS) for rapid heating under pressure to form dense nanostructured monolith

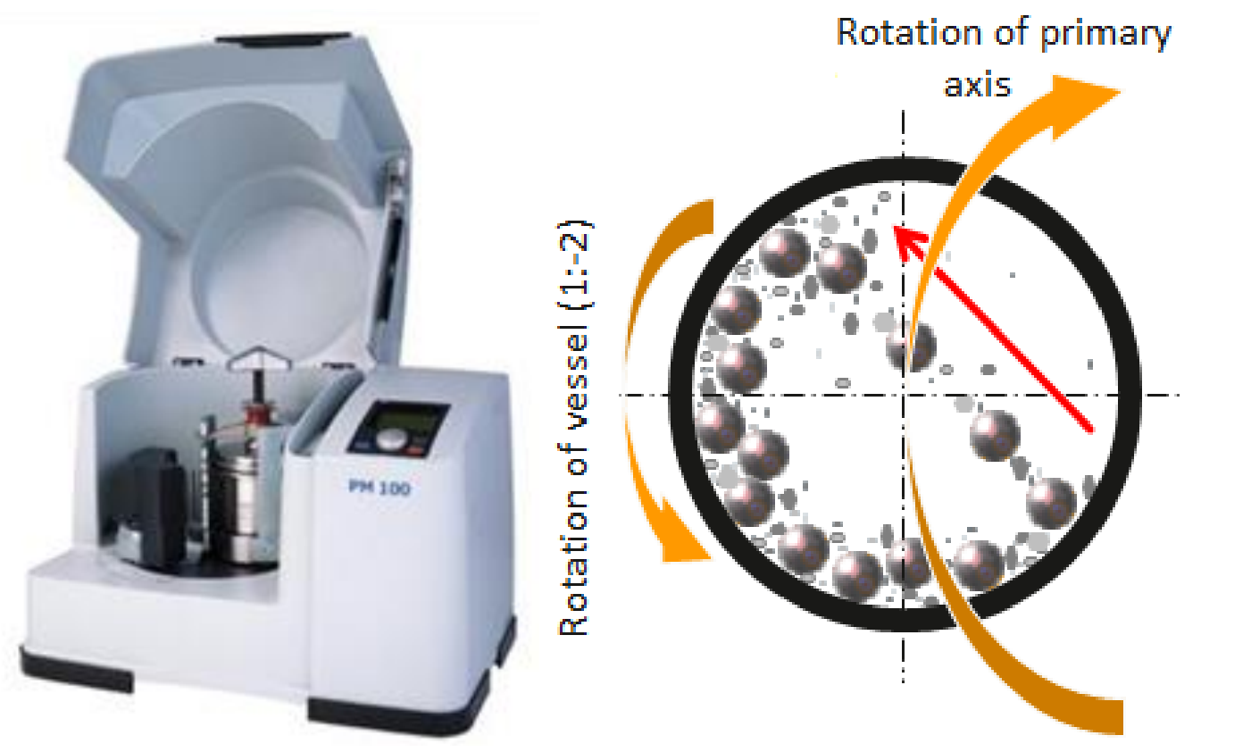


Figure 5. Planetary ball mill media cascades

High Energy Planetary Ball Milling
- Stoichiometric amounts of elemental powders
- Mill at 500 rpm for 24 hours in stainless steel 250 mL vessel filled with inert argon gas and 5 mm diameter steel media (440C) in argon
- 15:1 (media:powder) charge ratio

Spark Plasma Sintering
- Ramp 100 $^{\circ C}/_{min}$ to 800-1050 °C under 50 MPa
- Sintered under vacuum in graphite foil
- Cooled naturally to ambient temperature

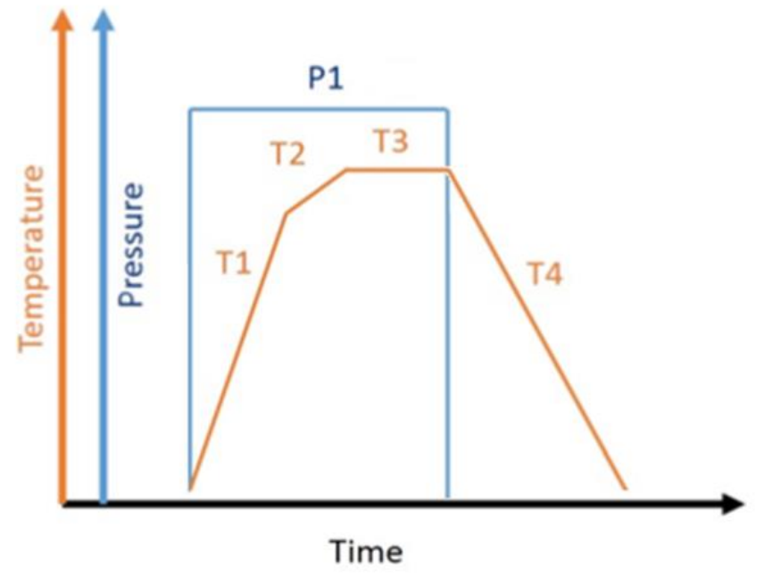
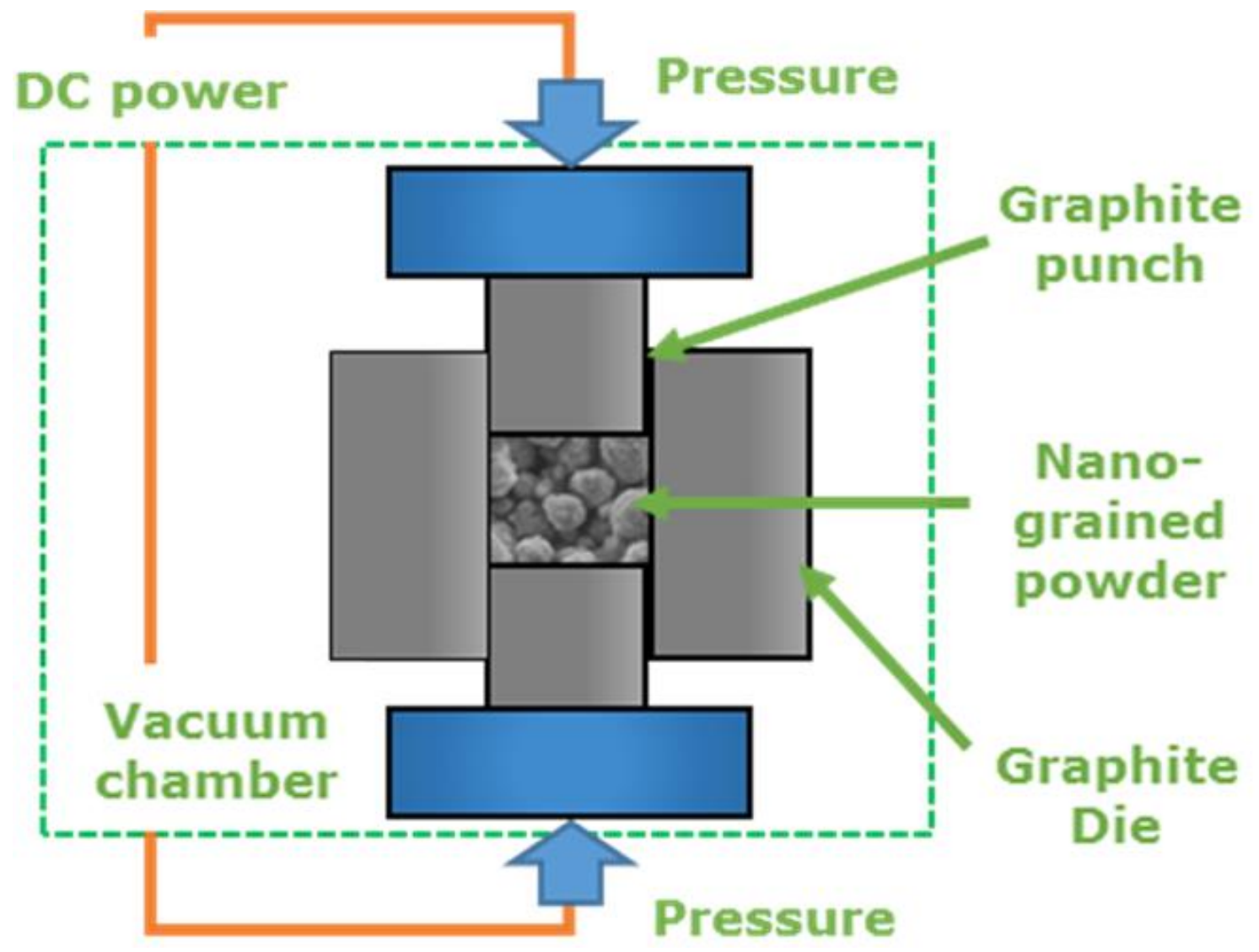


Figure 6. (left) Schematic sintering profile, (right) SPS sintering operation under vacuum and pulsed DC current



Results: Powder Characterization of $Ti_{0.75}Zr_{0.25}NiSn_{0.98}Sb_{0.02}$

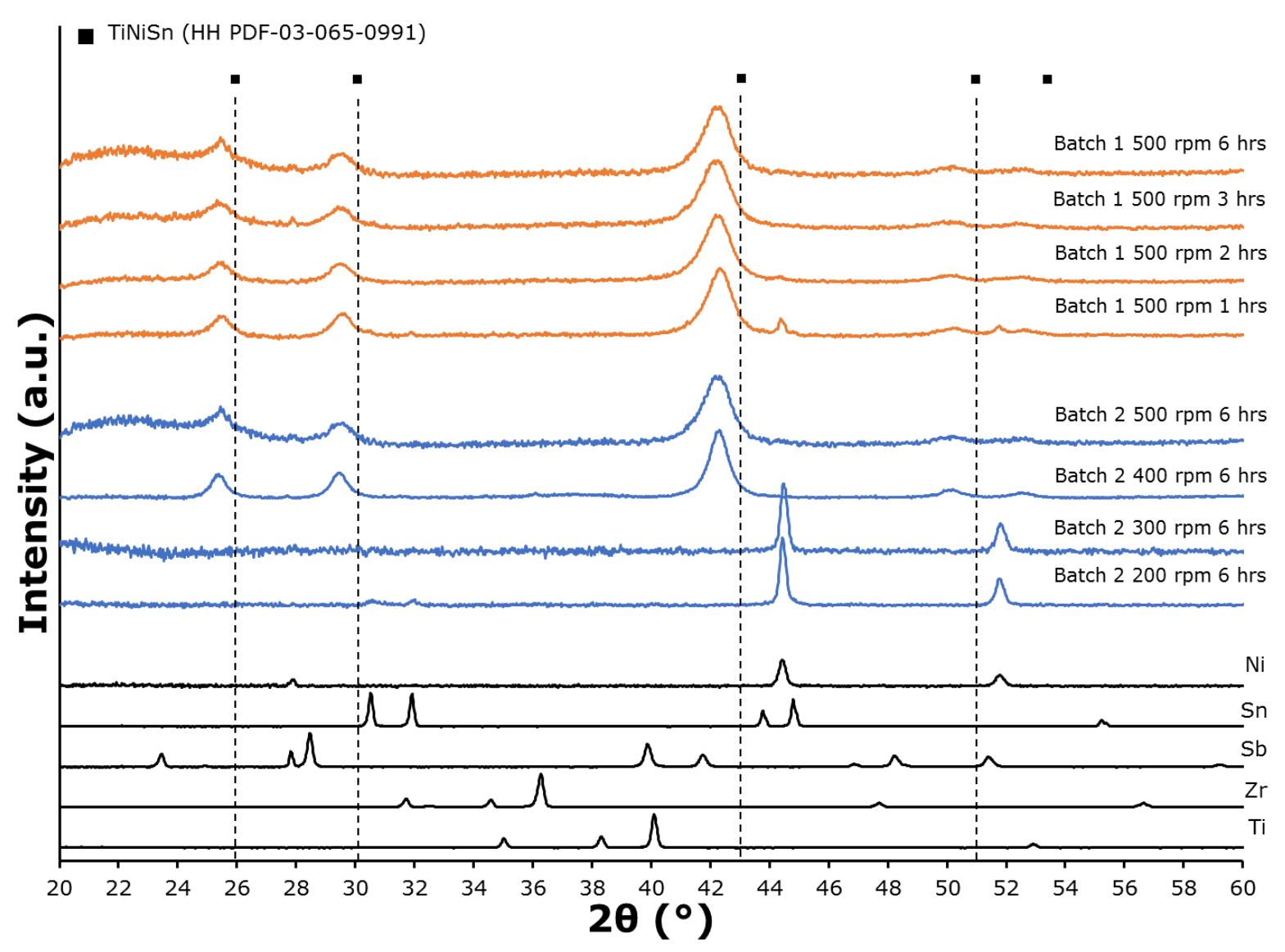


Figure 7. Powder XRD shows 400 rpm and 6 hours of milling to obtain single phase half-heusler

Powder X-ray Diffraction (XRD)
- Phases (minimum energy for HH formation)
- Peaks broaden (crystallite size decreases) with longer milling times, higher energy)
- Patterns shift due to strain, Zr substitution for Ti

Laser Scattering Particle Size Analysis (PSA)
- Suspension stability optimized with surfactants, dispersants, and ultra-sonication
- Spherical morphology distribution mean at 5 μm

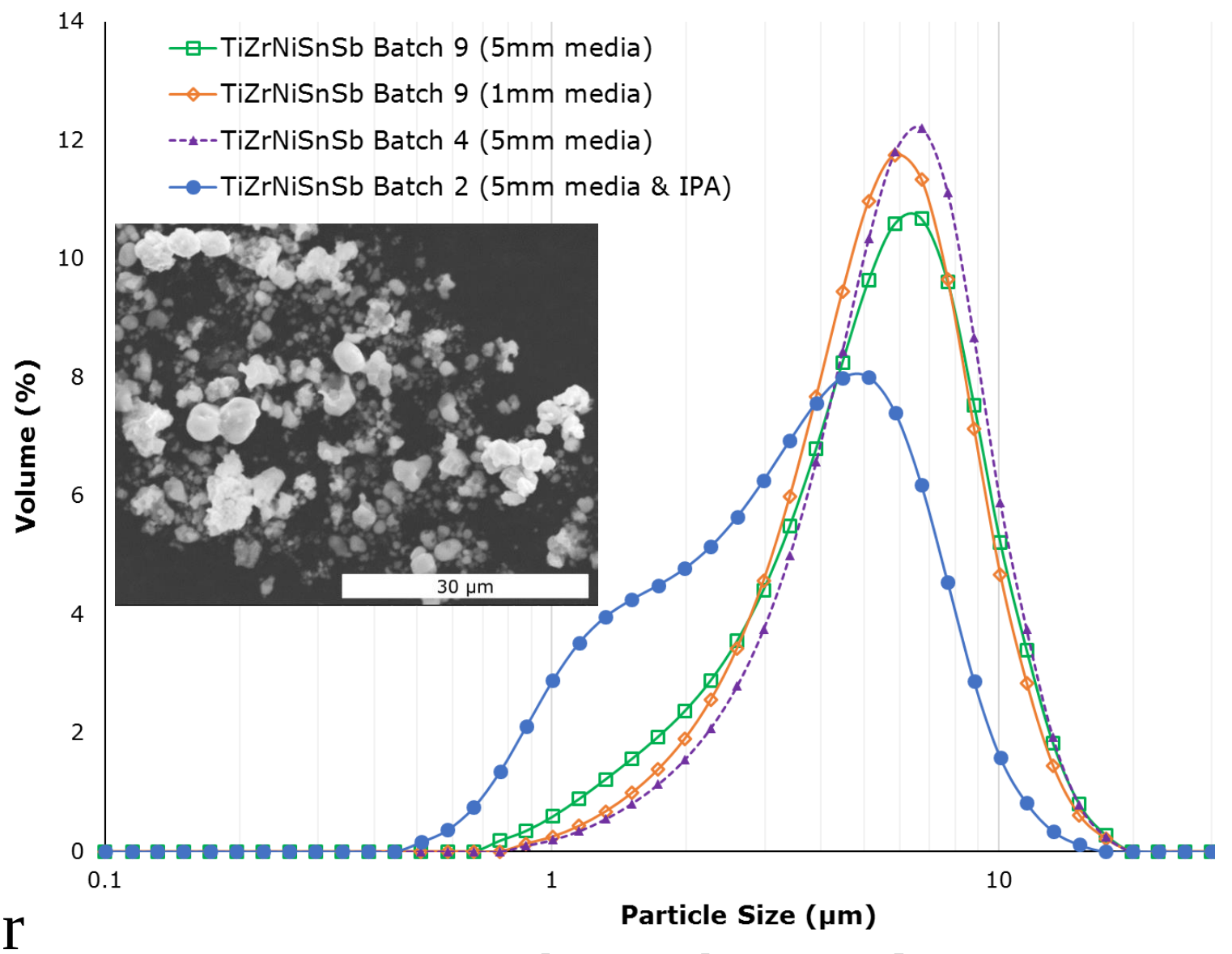


Figure 8. PSA shows changes due to wet milling; SEM shows spherical morphology

Results: Homogeneity and Composition of $Ti_{0.75}Zr_{0.25}NiSn_{0.98}Sb_{0.02}$

Energy Dispersive Spectroscopy (EDS)
- Verified HH 1:1:1 stoichiometry
- Nearly homogeneous but contains:
  - Iron contamination from steel media
  - Zirconium oxide inclusions
  - Deleterious unreacted Ti, Ni, Sn

EDS (Atomic %)	Ti	Zr	Ni	Sn	Sb
Target	24.75	8.25	33.00	32.34	0.66
Pellet Batch 1	26	8	35	31	1
Pellet Batch 2	25	8	34	33	1

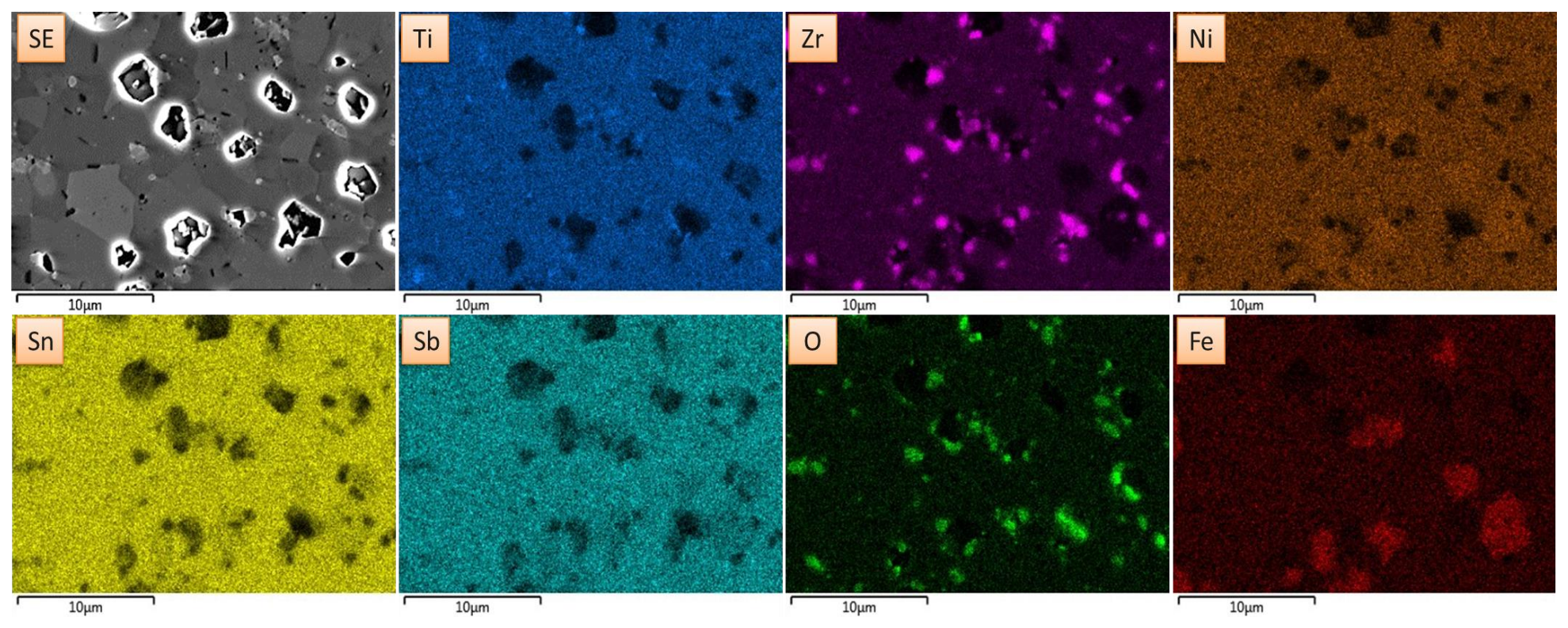


Figure 9. EDS maps on sintered pellet indicates ZrO_2 inclusions & iron contamination from milling process

Results: Grain Size and Phase of $Ti_{0.75}Zr_{0.25}NiSn_{0.98}Sb_{0.02}$

Sintered Grain Size and Thermal Treatments
- Create nanometer/micrometer grain sizes
- Treat at 1000 °C for 2 weeks for grain growth

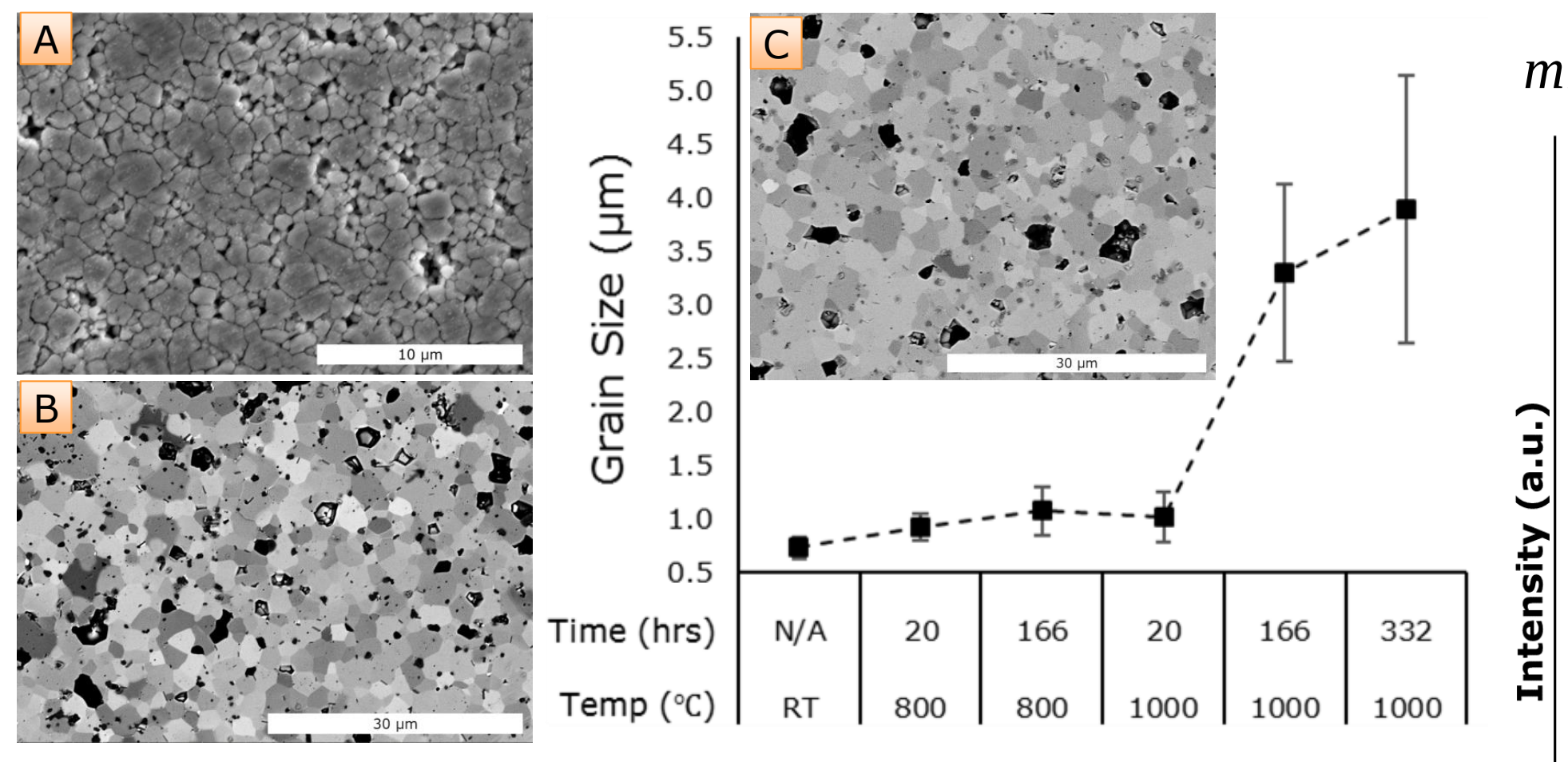
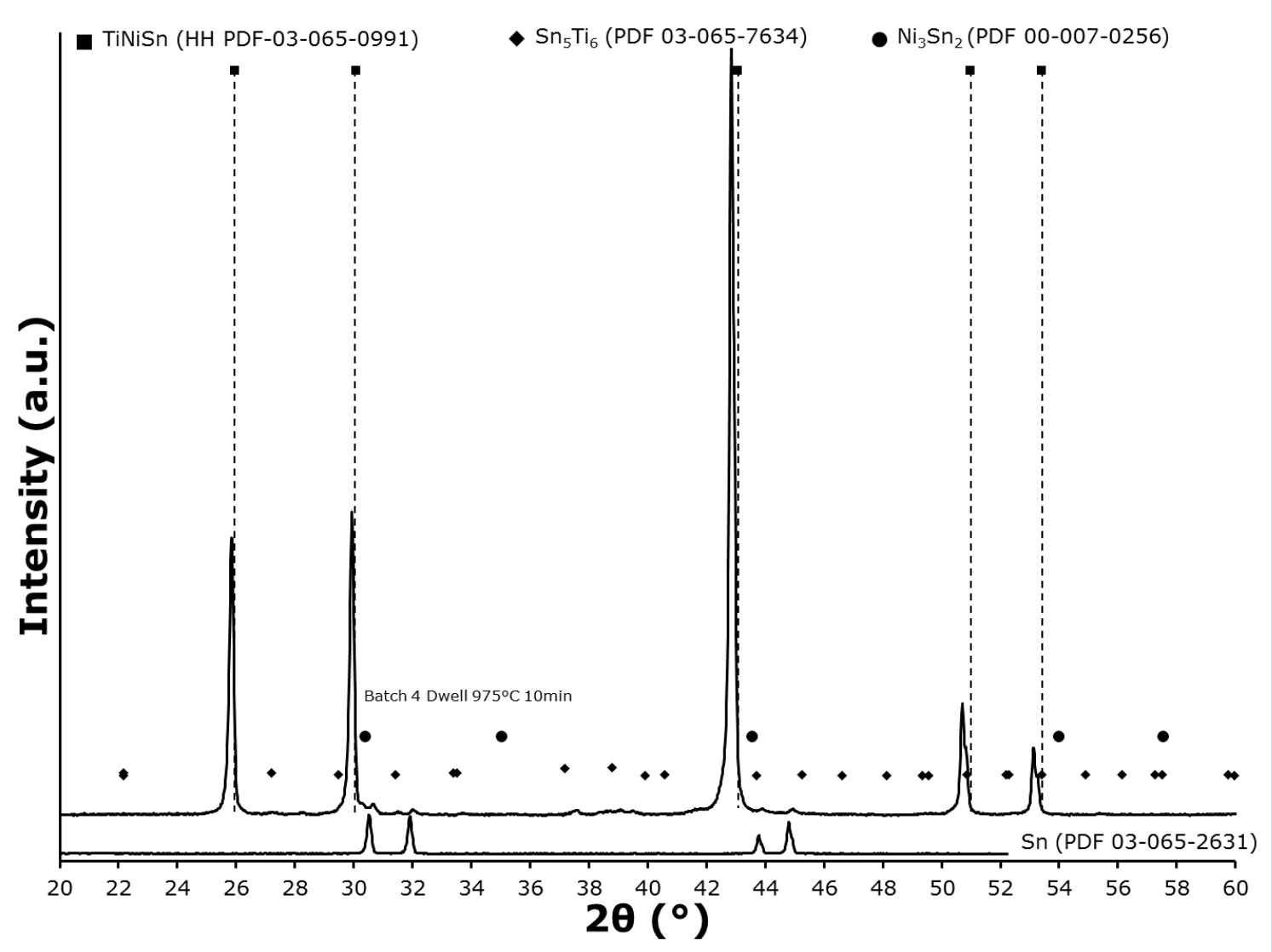


Figure 10. SEM images (A) SPS at 975 °C 10 minutes, etched (B) SPS at 1050 °C 2 minutes, unetched, (C) 975 °C sample treated 2 weeks at 1000 °C, unetched; Visible micrometer porosity ≈ 4%

Pellet XRD for Phase Identification

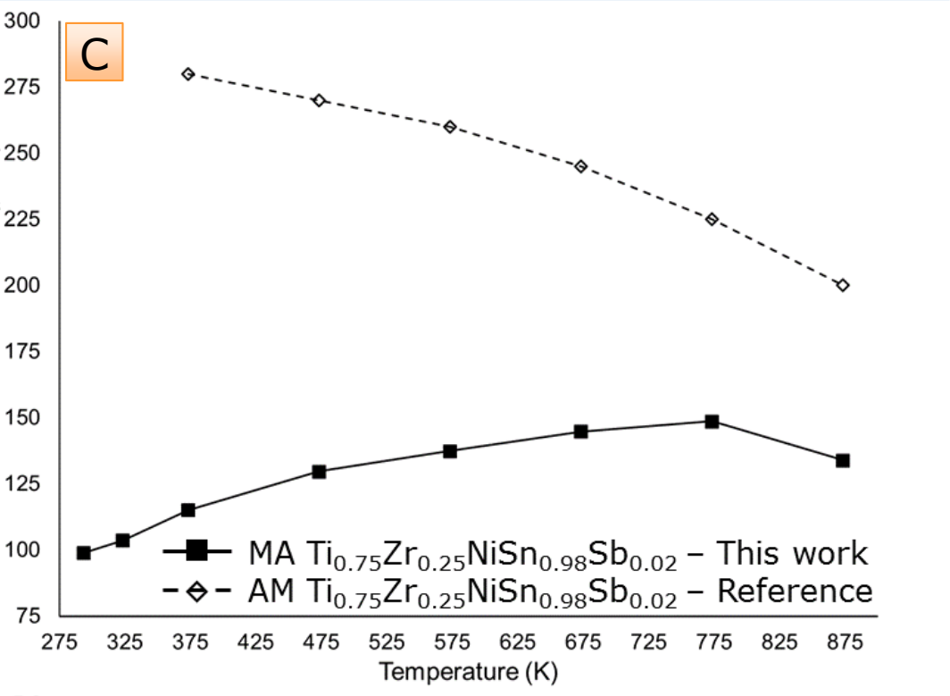
Figure 11. Pellet XRD of SPS at 975 °C for 10 minutes matches TiNiSn half-heusler reference, nearly single-phase purity obtained from ball milling; Impurity peaks are tin binary compounds

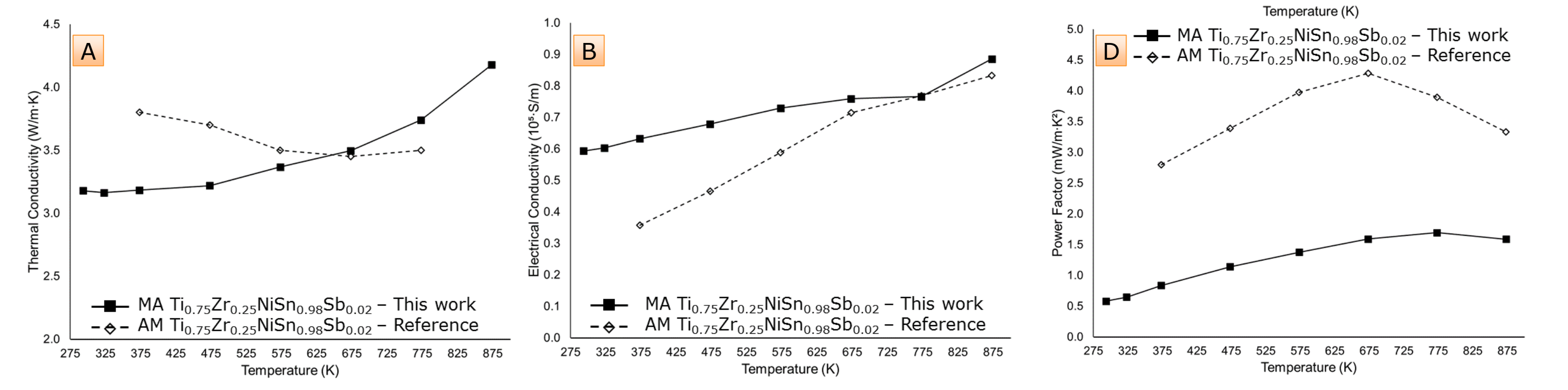


Results: Thermoelectric Performance

Comparison of Mechanical Alloy (MA) to Arc-Melt (AM) synthesis routes – MA can produce submicron grain sizes not typically seen in AM products

Figure 12. As temperature increases (A) thermal conductivity increases (B) electrical conductivity increases, (C) seebeck increases to a peak then decreases, (D) power factor increases; the reduced seebeck has a direct impact on the power factor and ZT. Reference data for the same composition synthesized using arc-melting and SPS taken from ref [3] (dotted lines with open diamonds). Lines are aids for the eye to see trends





Laser Flash Analysis (LFA)
- Thermal diffusivity on 12 mm disks
- Comparable thermal conductivity

$$ZT = \frac{S^2\sigma}{K}T$$

Seebeck & Electrical Resistivity (LSR)
- Seebeck & resistivity on 12 mm disks
- Comparable electrical conductivity
- Decreased seebeck (≈60%) and power factor (≈ 60%)

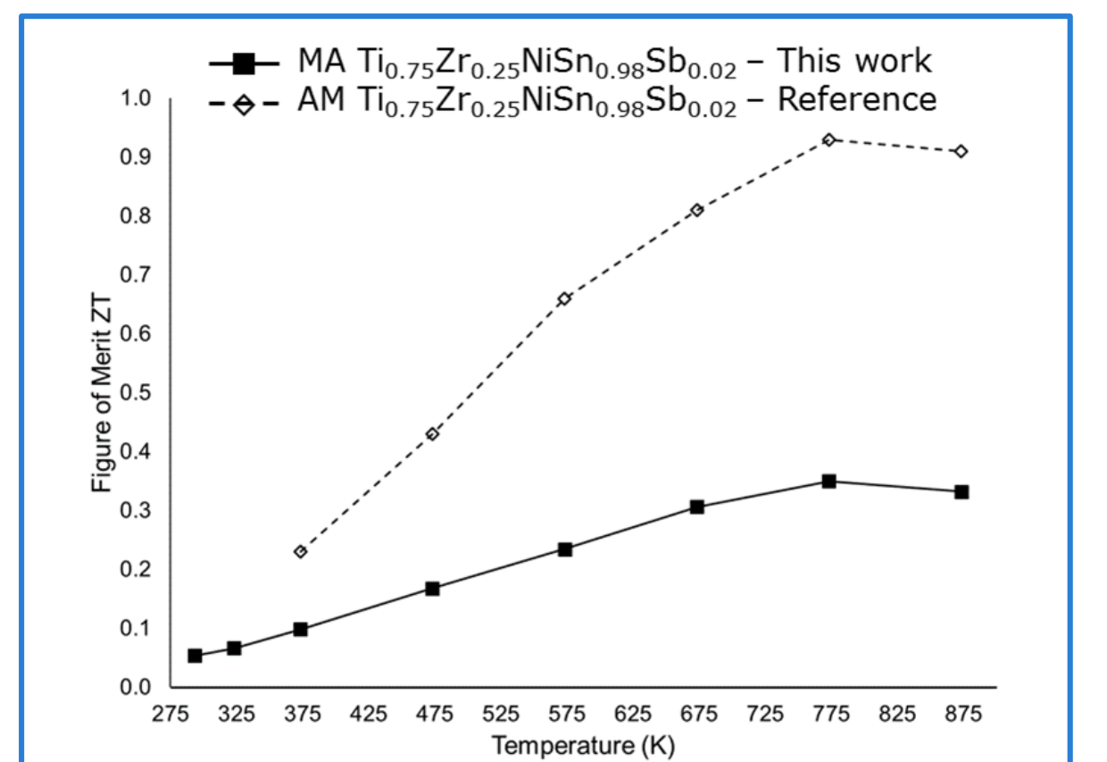


Figure 13. ZT for n-type half-heusler

Conclusion & Future Work

Figure of Merit ZT
- Peak ZT of 0.35 obtained for mechanically alloyed $Ti_{0.75}Zr_{0.25}NiSn_{0.98}Sb_{0.02}$ half-heusler
- Decreased peak ZT (~60%) for ball milled versus conventional arc-melted synthesis route
- Milling media contamination, ZrO_2 from oxygen ingress, and unreacted Ni, Ti, Sn affect carrier concentration & mobility & seebeck negatively for n-type
- Successfully alloyed Zr and Ti via ball milling; produced submicron grain size distribution

Future Work
- Milling with WC or ZrO_2 vessel/media for reduced contamination, increased milling efficiency
- Proton irradiation resistance as a function grain sizes

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References

[1] Casper et al, Semicond. Sci. Technol. 27, 063001 (2012)
[2] Gayner et al, Prog. Mater. Sci. 83, 330–382 (2016)
[3] Gürth et al, Acta Materialia. 104, 210-222 (2016)

Acknowledgements
This work was partially funded through the United States Department of Energy, Office of Nuclear Energy, Award DENE0008255
Special Thanks To:
Bryan Forsmann, CAES; Joe Croteau, BSU

U.S. DEPARTMENT OF ENERGY