Investigating the influence of synthesis procedure on the microstructure and thermoelectric properties for higher manganese silicide

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Higher manganese silicide (HMS) has been considered as an environment-friendly thermoelectric material due to its abundant elements. The developed technology for high quality feedstock materials, particularly for Si, leads to the possibility for a large scale production. In this presentation, we compare three different approaches for producing HMS samples, namely melt-cast (MC), which is a widely-used matured industrial procedure for silicon and other alloy production industry, spark plasma sintering (SPS) which has been mostly reported for lab-scale fabrication of HMS samples, and hot-pressing (HP) for a small scale synthesis. Feedstock is ElkemSolar ESS® with a purity of 99.999%. Ge has been added to form $MnSi_{1.75-x}Ge_x$ (x = 0.005 and 0.01) for altering the electronic properties. The results provide a base study for the future improvement.

Methodology and sample overview

Melt-cast (MC)	Sample ID
Undoped	AC-Ge00
x = 0.005	AC-Ge005
X = 0.01	AC-Ge01

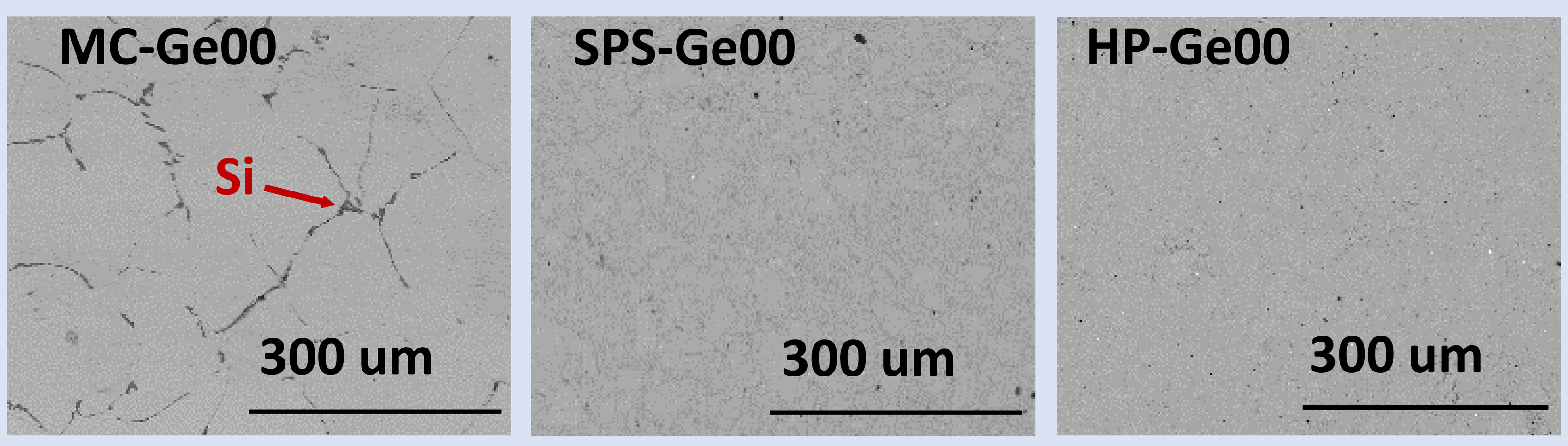
Sparkle plasma sintering (SPS)	Sample ID
Undoped	SPS-Ge00
x = 0.005	SPS-Ge005
X = 0.01	SPS-Ge01

Hot-pressing (HP)	Sample ID
Undoped	HP-Ge00
x = 0.005	HP-Ge005
X = 0.01	HP-Ge01

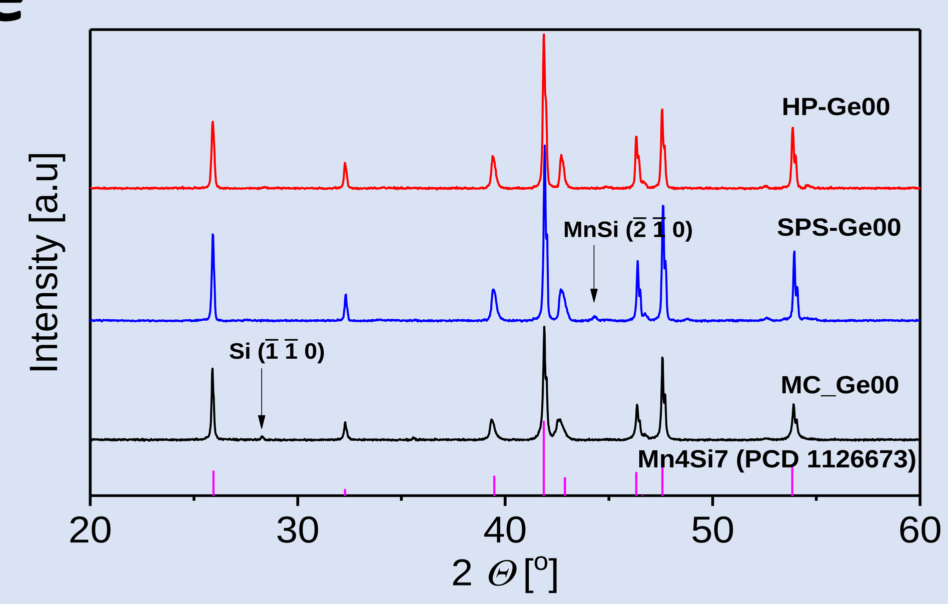
MC		MC	SPS	HP
Ingot	Melt	Ar flow		
	Solidification	Cast in graphite mold in air		
Pulverization	Milling	--	Swing mill* (Ar, 1400 rpm 90 s)	Plenary ball-mill ** (Ar, 300 rpm 50 hrs)
	Mean grain size (FWHM)	--	≈120 nm	≈15 nm
Consolidation	Mechanisms	--	Sintering via local heat induced by pulsed current passing through powder (850 °C, 90 Mpa) ***	Uniform temperature in induction furnace(950 °C. 60 Mpa) ****
	Mean grain size (FWHM)	> 10 μm	≈335 nm	≈179 nm

* Local heat reach above 100 °C due to high rpm. Part of raw material with low melting point lost.
** Lower local heat, < 50 °C. Contamination from jar due to long milling time.
*** Risk of local heat, peritectic reaction may occur at particular grain boundaries.
**** Incomplete densification due to limited pressure and low local heat

Influence of synthesis routes on microstructure

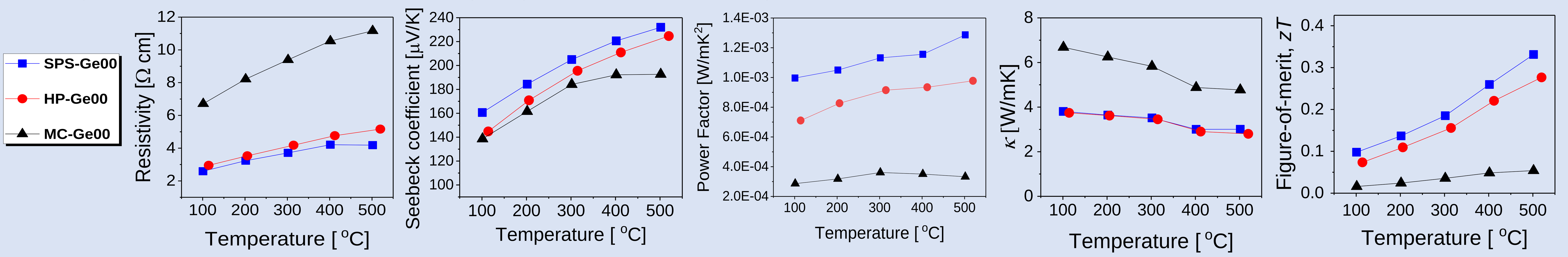


Relative density 96.1% Relative density 97.7% Relative density 97.3%



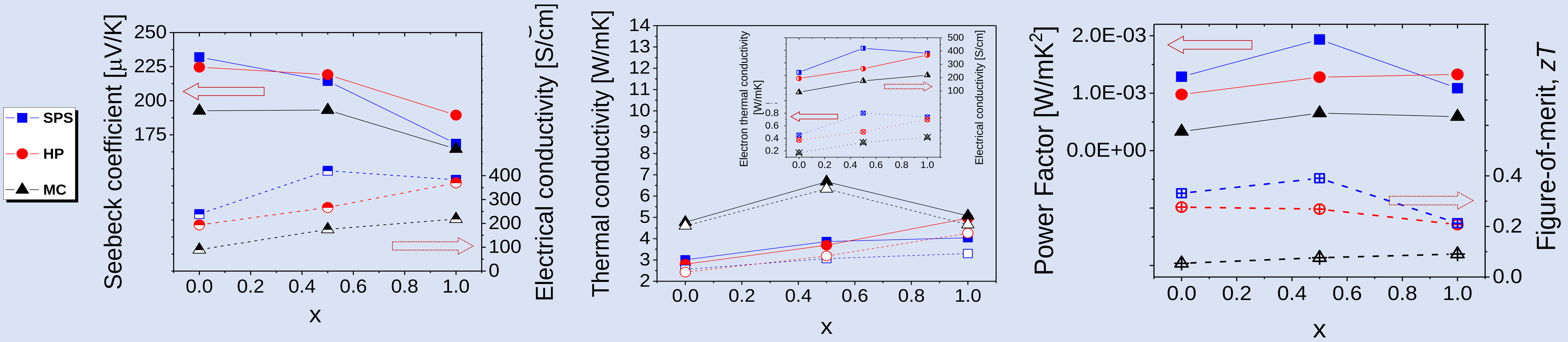
- MC-HMS samples are solidified from melts directly, Si segregations are observed by both SEM and XRD.
- SPS-HMS samples has been swing-milled and subjected to 850 °C. Small mount of MnSi was formed.
- HP-HMS samples has been sintered and annealed at 950 °C for 30 mins, dissolving the secondary phases.

Comparison in thermoelectric properties for undoped HMS



- High resistivity in MC- sampels is mainly due to micro-crack, while SPS- and HP- samples are highly compacted.
- SPS-samples offer the best Seebeck coefficient that is dominating the power factor.
- Thermal conductivity in MC-samples are much higher due to the contribution of Si-phase.

Doping effect (TE properties vs. x in $MnSi_{1.75-x}Ge_x$ at 500 °C)



Concluding remarks

We present how and microstructure changes when employing different synthesis approaches. The electrical conductivity and thermal conductivity are strongly dependent on the microstructure, which is resulted by the synthesis route. SPS offers the most dense structure, thus the best thermoelectric properties. The Seebeck coefficient shows a dependency on the doping level. The SPS $MnSi_{1.75-x}Ge_x$ with x = 0.005 yields the highest power factor, thereby figure of merit, due to the increased electrical conductivity. **The present work is funded by the Research Council of Norway project No. 69326.**