Conference or Workshop Item:

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Anomalous compound formation in Si-Ge thermoelectric materials

Liquid Metal Engineering Hub
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Introduction

Little research has been conducted on $Si_{1-X}Ge_X$ thermoelectric alloys. Specifically, what has not been investigated is the segregation behaviour and the formation of odd stoichiometric regions in the grain boundaries. Based on the equilibrium phase diagram, Si-Ge is described as a simple (random) solid-solution across the whole composition range. The Si-Ge phase diagram tells us that towards the end of solidification, we should be getting more Ge rich, but in a continuous manner (essentially, a continuous decrease in Si and a continuous increase in Ge).

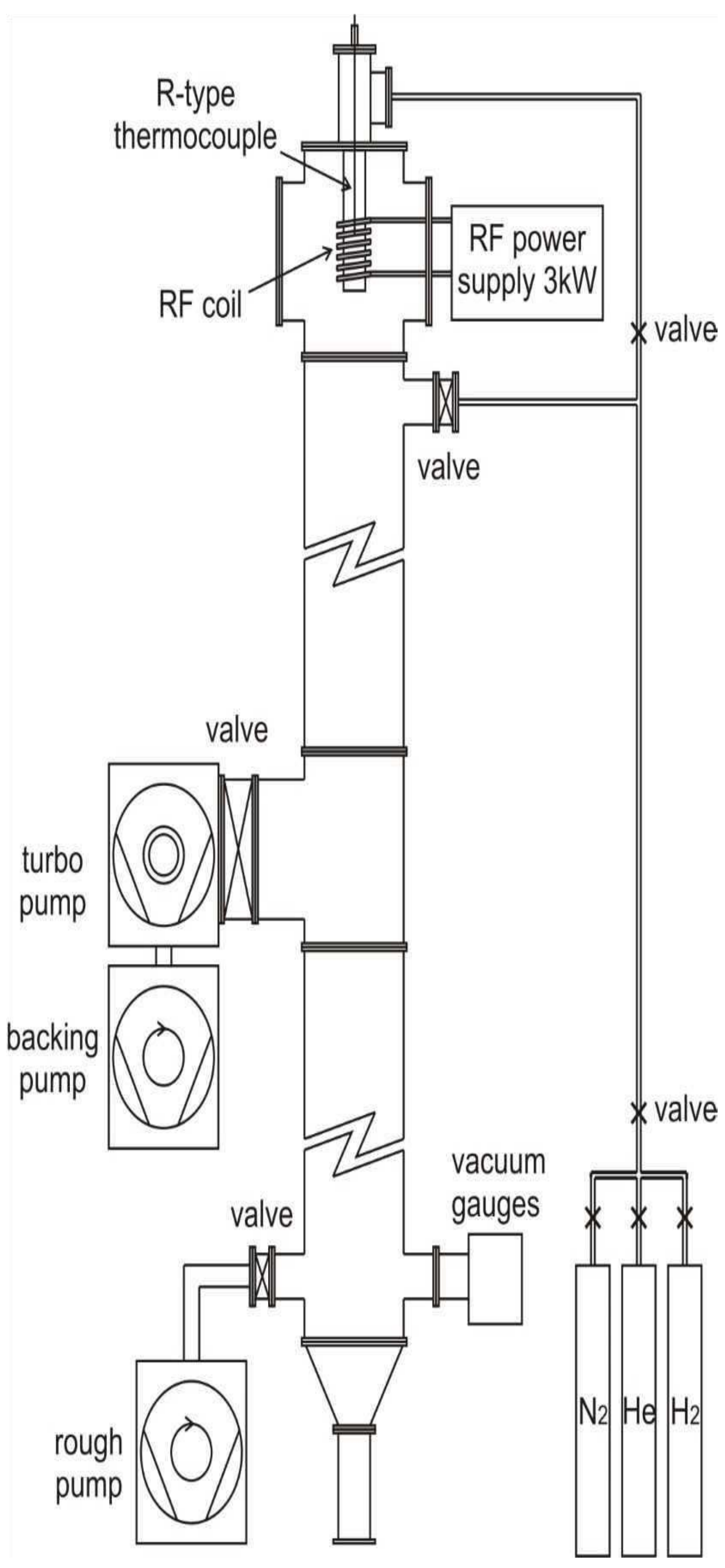
Observed regions of preferred stoichiometry, in which the Si:Ge ratio adopts simple integer ratios, are anomalous and indicative of chemical ordering, although no such ordering is expected or reported in Si-Ge. The key point here is to characterise any compounds formed at the grain boundaries, which might be a manifestation of phase separation. This phenomena might seem more consistent with the thermodynamics of the Si-Ge system, but it does not account for the Si:Ge simple integer ratios. In this research, we plan to produce/observe these regions and then identify a mechanism for this effect, something that has not been extensively explored before. This is being studied based on technological considerations which suggest that a good thermoelectric material should be chemically homogeneous.

Powder Fabrication by the Drop Tube Facility

In this work, the 6.5m high vacuum drop tube apparatus is employed to obtain powders from the directionally solidified $Si_{70}Ge_{30}$ (i.e., Si–14.2 at.% Ge) alloy by melting it using a 3 kW Radiofrequency (RF) coil.

In general, the DT run includes three main stages which are; sample mounting, vacuum pumping and melting. First, a total mass (4 gram) of starting alloy was loaded into the alumina crucible which has three laser-drilled holes in the bottom each hole is about 300µm, these holes allow the melt ejection. The vacuum procedure tends to ensure that an oxygen and moisture free atmosphere is achieved into which the liquid is ejected and sprayed.

During the melting, an R-type thermocouple was used to record the temperature gradient within the melt crucible. To ensure reaching to the melting temperature, the estimated 50 K superheat was used for the duration of a 130min heating cycle (total heating time) before the melt ejection from three micro-holes in the base of the crucible by pressurising it by 4 bar of N_2 gas. As the molten droplets solidify rapidly during the free-falling, the smaller droplets will cool more rapidly. After cooling therefore this giving different sized-powders which are collected at the bottom catch-pot of the drop tube. Finally, the powders were sieved such that they were divided into standard sized-groups of 75, 106, 150, 212, 300, 500 and 850µm.



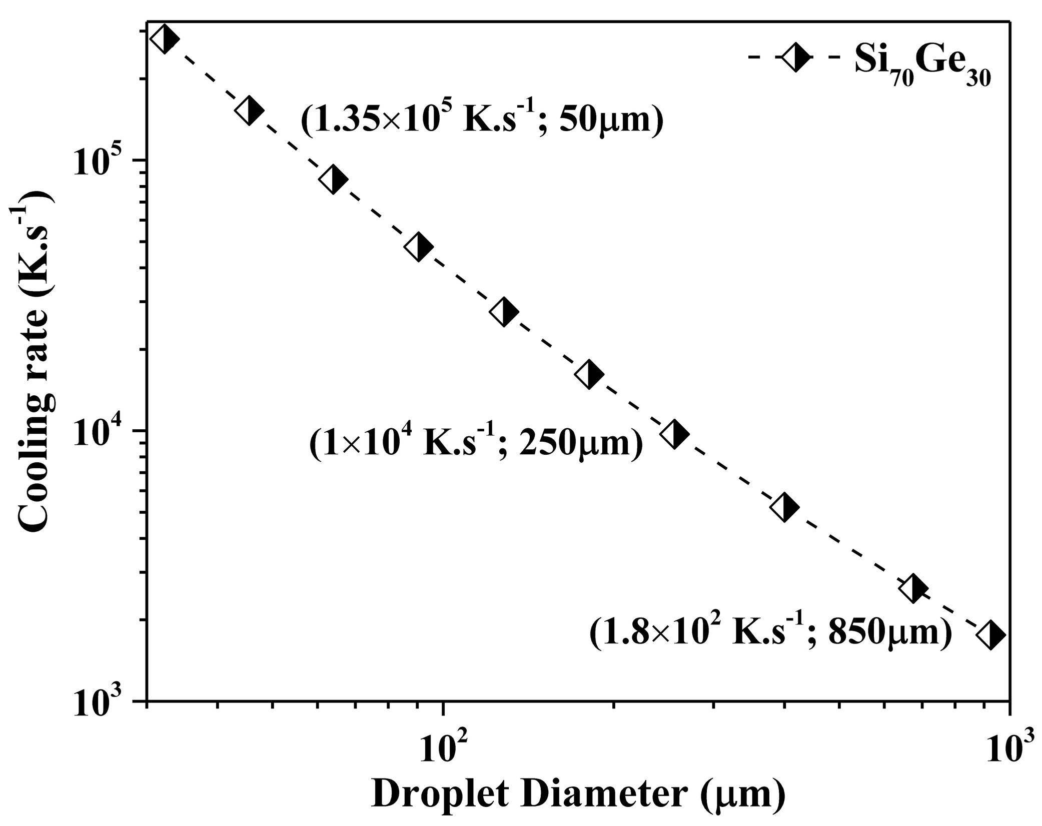
The $Si_{70}Ge_{30}$ powders are then hot-mounted, ground and polished in order to characterize the obtained microstructures and allow a relation to be studied between cooling rates and properties. In this work, one size fraction (300-500µm) droplet was selected for material characterization using SEM-EDX.

Cooling rate estimation

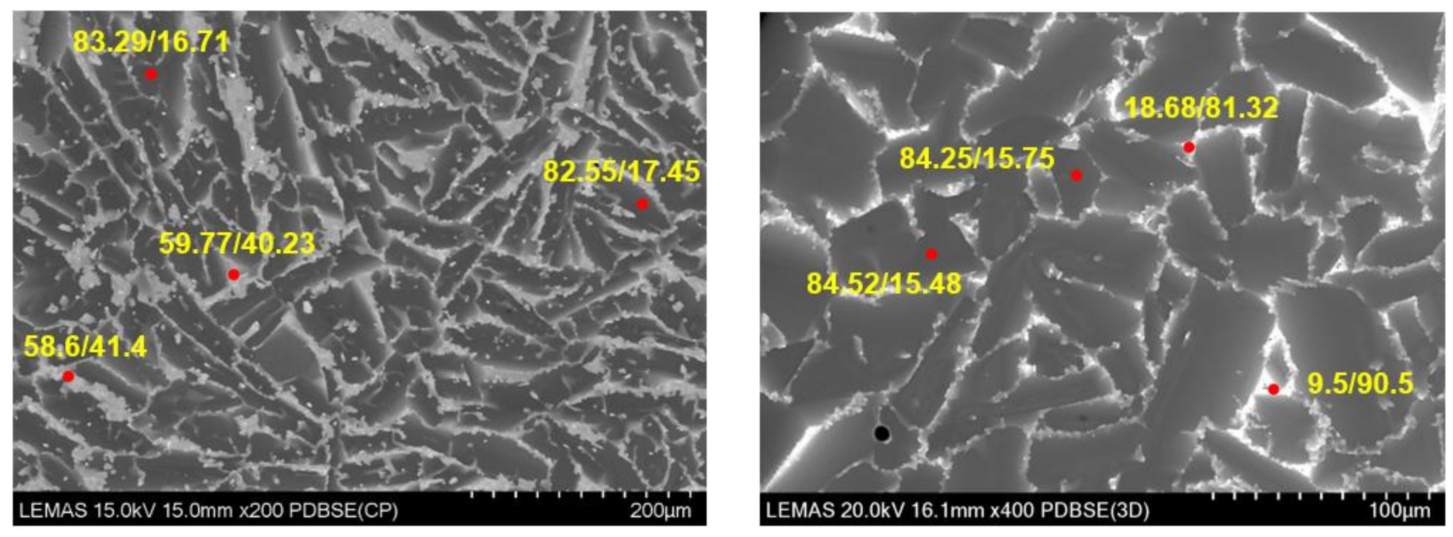
The cooling rate of freely falling droplets in the drop tube can be estimated by:

$$\dot{T} = \frac{6}{\rho C_p d}\left[\varepsilon\sigma\left(T^4 - T_a^4\right) + h\left(T - T_a\right)\right]$$

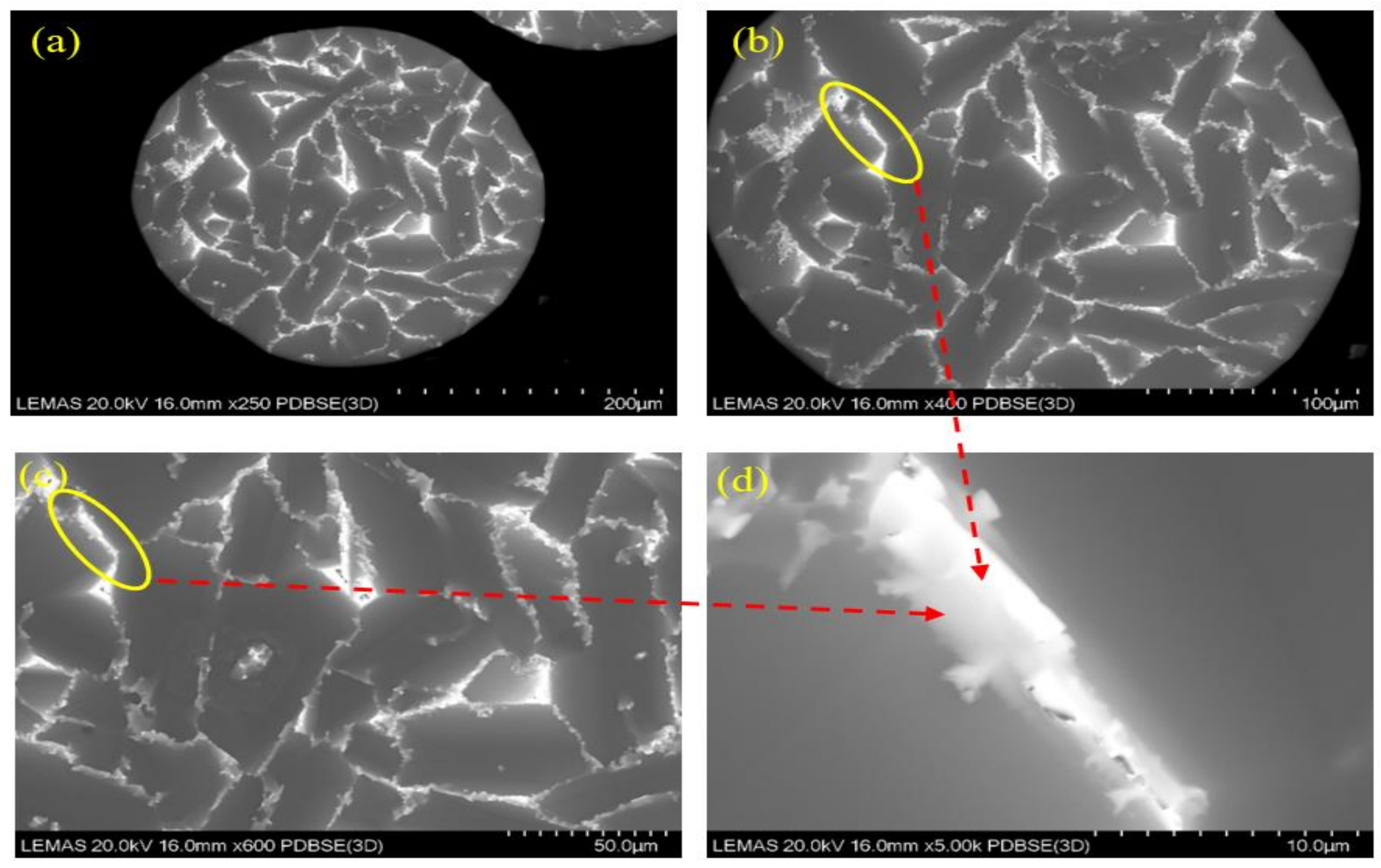
- The droplet diameter decreases as the cooling rate increases.
- Si-30 wt.% Ge (14.2 at. % Ge) alloy has been subjected to rapid solidification, with the resulting droplets of size 300-500µm being subject to cooling rates that equate to 4200-8400 K s⁻¹.



Results



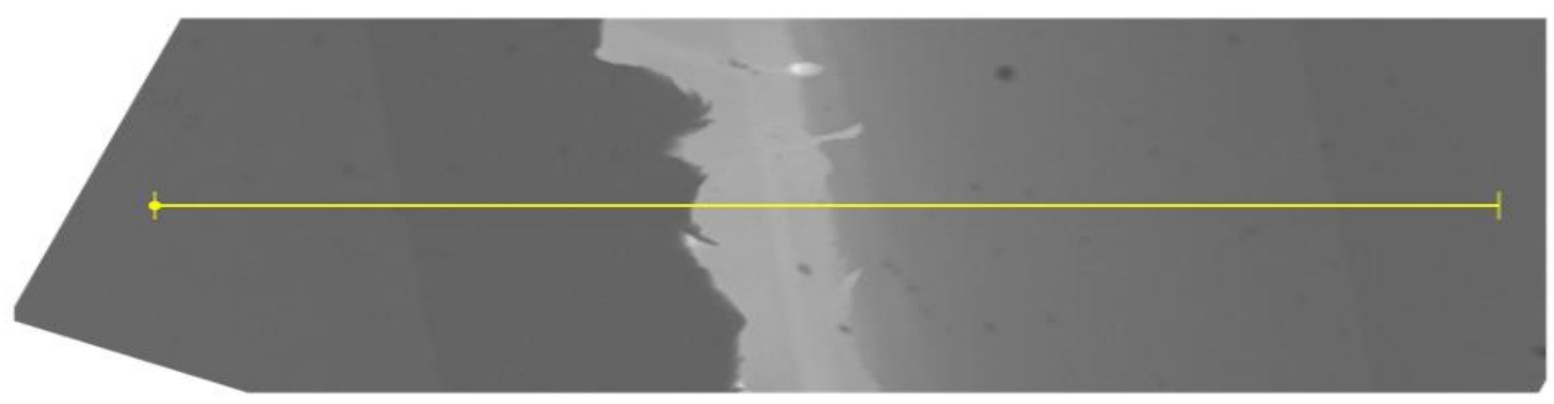
SEM-BSE micrographs with EDX point measurements (Si/Ge in wt. %) of Starting $Si_{70}Ge_{30}$ material (left) and DT material (300-500µm) (right), showing unexpected severe solute segregation across the grain boundaries is observed for the rapidly solidified material.

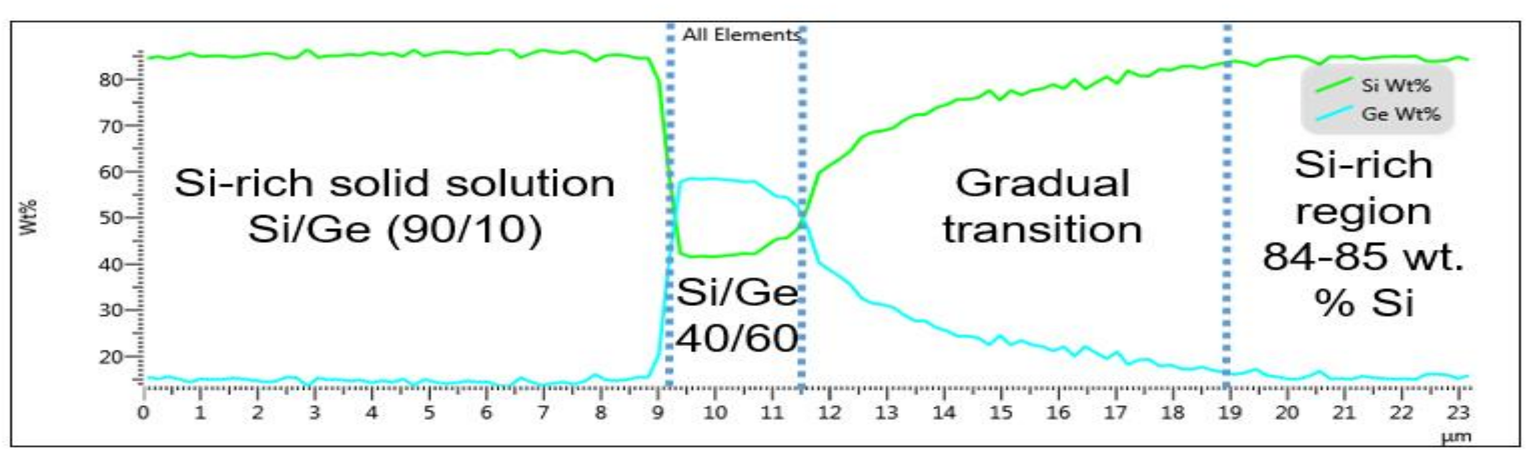


SEM-BSE micrographs displaying a typical morphology of droplet (300-500µm) and the appearance of bright distinct Ge-rich grain boundaries as marked by yellow ring.

EDX line measurements

- There are four discrete greyscale levels.
- On the left of the micrograph below, the first distinct region is the Si-rich solid solution.
- The other region on the right of the micrograph is the Si-rich region, which is consistent the EDX point measurements.
- The region from the distance ~11.5µm onwards until ~19µm, it appears to show a gradual transition across this region.
- The intermediate region is selected as the area of interest, an odd region with preferred stoichiometry found (~ Si-60 wt.% Ge, where the Ge:Si ratio seems to adopt a simple integer ratio i.e., Ge3Si2).





Greyscale analysis by ImageJ

- As the backscattered electrons come from a rather smaller region (i.e., less width and less depth), the greyscale analysis may give a little more precision.
- It appears that there are number of distinct peaks in the histogram profile which seem to conform to regions of discrete contrast in the image.
- This would support the observation of different lattice parameters.