Crystal growth of $FeSb_2$ and $CoSb_3$ by a modified Bridgman technique

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Materials to be used in thermoelectric devices, e.g. to directly transform waste heat into electric power, should have a high Seebeck coefficient and high electrical, but low thermal conductivity. $FeSb_2$ and $CoSb_3$ and third-component modifications based on them are among the thermoelectric materials discussed today for future applications [1, 2]. The main advantages compared to the present record holders like PbTe are the better availability and less toxicity of the constituting metals.

$FeSb_2$ (marcasite-type structure) and $CoSb_3$ (skutterudite-type structure) are peritec-tically melting compounds with decomposition temperatures of 750°C and 874°C, respectively. Thus, they cannot be crystallized from congruent melts but have to be grown below the peritectic temperature from Sb-rich solutions of more than 90 at.% Sb. Because of the relatively high Sb vapour pressure, crystal growth has to be carried out in closed ampoules, e.g. using the Bridgman method from a high-temperature solution. Unfortunately, liquid-phase mixing in closed Bridgman-type ampoules is not easily to be achieved, but would be a prerequisite to remove the rejected Sb excess from the growing phase boundary as to avoid second-phase inclusion formation of pure Sb into the growing crystal.

In vertical Bridgman growth of $FeSb_2$ and $CoSb_3$ we found a high amount of Sb inclusions even using very low growth rates of less than 1 mm/day, demonstrating the necessity of some mechanism of liquid-phase mixing, additional to the weak contri-bution of natural convection. Even in experiments using a Bridgman configuration being inclined with respect to the axis of gravity, buoyancy-driven convection could not be remarkably increased to avoid second-phase inclusions. That is, why we added a continuous rotation of the growth ampoule to the inclination of the Bridgman furnace. With a Bridgman-type set-up being tilted by 15° against the horizontal, the growing crystal rotates together with the ampoule while the Sb-rich liquid tries to keep its horizontal surface level. This results in a strongly forced convection within the solution, especially next to the growth interface where materials transport is needed most as to prevent the system from constitutional supercooling.

Synthesis and crystal growth conditions will be discussed in this talk as well as results of the phase characterization by optical microscopy and X-ray diffraction. First experiments using this modified Bridgman growth technique resulted in single-phase ingots of $FeSb_2$ and $CoSb_3$, but so far not in single crystals of these compounds. This will be the next goal to be achieved by introducing native seeding.

The advantage of this modified growth technique is not at all restricted to the Sb-based thermoelectric materials but may be a powerful approach in unidirectional freezing from off-stoichiometric melts, in general.

[1] P. Sun, N. Oeschler, S. Johnsen, B.B. Iversen, F. Steglich, Dalton Trans. **39** (2010), 1012-1019.
[2] Y. Kawaharada, K. Kurosaki, M. Uno, S. Yamamaka, J. Alloys Compd. **315** (2001), 193-197.