Ge and Mo containing precipitates in higher manganese silicide crystals

Mn$_4$Si$_7$

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Higher manganese silicides (HMS) MnSi$_{1.71-1.75}$ could attract more attention as potential high-temperature thermoelectric materials that are cheap and non-toxic [1]. However thin layers of cubic MnSi precipitates periodically distributed across the HMS crystals might contribute to some degradation of thermoelectric properties [2]. It was reported [3, 4] that HMS crystals grown by Bridgman method with Ge, Mo and Al impurities had better properties as well the amount of MnSi precipitates significantly reduced. Impurities in the HMS crystal lattice are believed can contribute to increasing the electrical conductivity and decreasing the thermal conductivity, and thus to the improvement of the thermoelectric performance. Investigation of structural features of doped crystals can help in optimization of crystal growth conditions.

This paper reports the results of electron microscopy study of Al, Ge, Mo doped HMS crystals with general formula of ((Mn$_{0.98}$Mo$_{0.02}$)[(Si$_{0.98}$Ge$_{0.02}$)$_{1.75}$]$_{0.99}$Al$_{0.01}$) grown by the Bridgman technique at 1473 K in Ar atmosphere.

Microstructures of as grown samples were examined by SEM and EBSD in a FEI QUANTA 200 3D microscope, and by TEM in a FEI TITAN 80-30 FEG electron microscope. Chemical composition was estimated by energy dispersive X-ray spectroscopy (EDS) in both SEM and TEM. Analysis of experimental data was done using Gatan Digital Micrograph, TSL OIM software package (EDAX) and JEMS [5] programs. Samples for TEM observations were prepared by FIB in a FEI QUANTA 200 3D microscope.

Electron diffraction patterns and EDS data showed the formation of tetragonal Mn$_4$Si$_7$ single crystals. No other Mn-Si phases with the stoichiometry of MnSi$_{1.71-1.75}$ were observed. The crystal matrix contains 1.5 at% Ge, 0.5 at% Al and 0.5 at% Mo. In addition, Ge and Mo containing precipitates of different shape and sizes were found: tetragonal MoSi$_2$ crystals of micron- and submicron-scale sizes and precipitates of Si-Ge solid solution with different Si/Ge ratio. Aluminum oxide was observed mainly in the pores of the matrix.

Orientation relationships between the Mn$_4$Si$_7$ matrix and precipitates were investigated by electron backscatter diffraction in SEM (Fig.1) and transmission electron diffraction on submicron level and Fourier transform (HRTEM diffractograms) at the nanoscale (Fig.2). The following orientation relationship [100]$(010)$Mn$_4$Si$_7$||(112)$(110)$Si/Ge was observed more often. Doping resulted in suppression of the regular distribution of cubic MnSi precipitates in tetragonal crystals. Small rounded MnSi precipitates were found attached to areas with Si-Ge solid solutions.

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References

Figure 1. SEM image (BSE mode) of polished doped HMS crystal and EBSD patterns from the corresponding areas.

Figure 2. HRTEM image of the interphase boundary between the Mn$_4$Si$_7$ crystal and Si/Ge precipitate.