Thermoelectric materials based on Seebeck effect convert waste heat into electricity. The higher manganese silicide (HMS) is p-type thermoelectric material which exhibit figure of merit $ZT = 0.3-0.4$ at 700 K ($ZT = S\sigma T/\kappa$, $ZT$ – figure of merit, $S$ – Seebeck coefficient, $\sigma$ – electrical conductivity, $\kappa$ – thermal conductivity, $T$ – absolute temperature)\cite{1}. The thin layers of cubic MnSi precipitate periodically segregate across c-axis of HMS crystals and can contribute to some degradation of thermoelectric properties \cite{2}. The HMS crystals grown by Bridgman method with Ge, Mo and Al dopants had better properties as well the amount of MnSi precipitates significantly reduced \cite{3, 4}. It is believed that these dopants can contribute to increasing the electrical conductivity and decreasing the thermal conductivity, and thus to the improvement of the figure of merit. We report the results of electron microscopy study of Al, Ge, Mo doped HMS crystals with formula of $((\text{Mn}_{0.98}\text{Mo}_{0.02})[(\text{Si}_{0.98}\text{Ge}_{0.02})_{1.75}\text{Al}_{0.01}])$ grown by the Bridgman technique at 1473 K in Ar atmosphere. Microstructure of as grown samples has been examined by SEM and EBSD in a FEI QUANTA 200 3D microscope and by TEM in a FEI TITAN 80300 FEG electron microscope. Chemical composition has been estimated by energy dispersive X-ray spectroscopy (EDS) in SEM and TEM. Electron diffraction patterns and EDS data reveal the tetragonal Mn4Si7 matrix crystal. None other Mn-Si phases with the stoichiometry of MnS$_{1.171-1.75}$ are observed. The MnSi phase is not observed in doped HMS crystal. The addition of Al, Ge and Mo dopants results formation of silicon-germanium and silicon molybdenum precipitations with size from several nm to hundreds microns. The singe crystal Si-Ge precipitations show preferred orientation in relation to matrix crystal. The polycrystalline MoSi2 precipitations form a multicomponent texture along [001] Mn4Si, direction. Alumina is observed mainly in the matrix pores. Analysis of EDS data and electron diffraction patterns from HMS matrix crystal shows that dopants atoms randomly occupy sites at Si and Mo sublattice. The work was partly supported by the RFBR grant №12-02-31444 and grant NSh-2883.2012.5

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\textbf{Keywords:} electron microscopy and diffraction; precipitations