Present paper is devoted to results of research of formation nanostructure in monocrystals Bi2Te3 doped by 0.1 mass % tin and Bi2Te3-xSex (x = 0.04). The data of studying of obtained samples Bi2Te3 and Bi2Te3-xSex with use of electronic microscopy and X-ray diffraction method are resulted. The formation of nanodimensional layers of is established on surfaces (0001) of Bi2Te3 and Bi2Te3-xSex as "islands" comparable with the sizes of Van der Waals gaps of crystals. During the crystal growth as result of impurity diffusion along a surface (0001), the accumulation, redistribution and nanocrystal formation between Te(1)–Te(1) layers is occurring.