Crystal Structure Refinements of Ge($tP12$), Physical Properties and Pressure-induced Phase Transformation Ge($tP12$) ↔ Ge($tI4$)

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Single crystals of the modification Ge($tP12$) are prepared by compressing semiconductor-grade germanium to pressures above 11(1) GPa and heating to temperatures between 1200(100) and 1500(150) K before a stepwise cooling precedes a complete pressure release. The tetragonal crystal structure of Ge($tP12$) is refined by means of single crystal X-ray diffraction data collected at ambient conditions (a = 592.81(2), c = 698.03(3) pm, space group $P4_32_12$). The atomic arrangement comprising interconnected spiral chains of fourfold symmetry bears a structural similarity to the high-pressure modification S($tI16$). High-pressure ambient-temperature powder X-ray diffraction measurements reveal a significant anisotropy of the compressibility compatible with the selected crystal structure description. The determined bulk modulus of Ge($tP12$) amounts to 70(1) GPa which is in good agreement with theoretical calculations and similar to experimental values of other four-coordinated germanium allotropes. Ge($tP12$) is a diamagnetic semiconductor with $\chi_0 = -3.1(3) \cdot 10^{-7}$ emu g^{-1} and $\rho_{300\ K} \approx 6\ \Omega$ m at 300 K. At 10.1(3) GPa, the beginning of the formation of Ge($tI4$) indicates the onset of a structural transition. The two-phase region extends up to a maximum pressure of 13.0(5) GPa in the direction of increasing pressures. Upon stepwise decompression, the phase Ge($tP12$) is reformed from Ge($tI4$) at 9(1) GPa.

Key words: Germanium, High-pressure Modification, Single Crystal, Magnetic Properties, Electrical Resistivity