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Three new ternary mixed lanthanum stannide/germanides have been synthesized and characterized in the course of a systematic study of the phase formation at the 3 : 5, 3 : 4 and 1 : 1 pseudo-binary sections of the ternary system La - Ge - Sn, *i. e.* a study of the 'coloring' in mixed tetrelides. The structures of the title compounds have been determined using single-crystal X-ray data, and the electronic structure was analyzed by means of simple electron counting rules and FP-LAPW band structure methods. Even a very minor substitution of Sn by Ge in the 3 : 5 stannide La_3Sn_5 already changes the structure from the Pu_3Pd_5 type of the binary stannide towards the Tl_4PbTe_3 type ($\text{La}_3\text{Sn}_{4.4}\text{Ge}_{0.6}$: tetragonal, space group $I4/mcm$, $a = 861.35(10)$, $c = 1211.48(13)$ pm, $Z = 4$, $R1 = 0.0420$). According to the anionic building blocks present, isolated $[\text{Ge}/\text{Sn}]^{4-}$ anions and heavily puckered 4.8^2 nets of three-bonded tin atoms (*i. e.* $[\text{Sn}_4]^{4-}$ Zintl ions), a small formal electron excess (+9/−8) occurs, which is also apparent from the position of the minimum in the calculated tDOS. In contrast, starting from the known binary stannide La_3Sn_4 (orthorhombic, space group $Cmcm$, Er_3Ge_4 structure type) a substitution of tin by germanium is possible without a change of the structure type up to the border composition $\text{La}_3\text{Sn}_{3.1}\text{Ge}_{0.9}$ ($a = 448.61(5)$, $b = 1170.68(14)$, $c = 1556.0(2)$ pm, $Z = 4$, $R1 = 0.0380$). Germanium preferentially occupies the sites of the $[\text{Ge}/\text{Sn}]_3$ trimers, whereas the site of the square-planar coordinated Sn(3), which is stabilized by hypervalent bonding, is not populated by germanium. Taking the respective partial bonding into account, the Zintl electron count is also nearly exact (+9/−8). The new complex mixed tetrelide $\text{La}_9\text{Sn}_{6.7}\text{Ge}_{3.3}$ (tetragonal, space group $P4_2/ncm$, $a = 1602.04(3)$, $c = 1724.42(5)$ pm, $Z = 8$, $R1 = 0.0706$) exhibits nine crystallographically different tetrel positions, which are occupied by isolated Sn and Ge atoms, $[\text{Sn}/\text{Ge}]_2$ dumbbells, bent $[\text{Sn}_3]$ trimers, planar four-membered rings $[\text{Ge}_4]$, and planar six-membered rings $[\text{M}_6]$. In this compound, the electron count following the Zintl concept also reveals only a very small formal excess of electrons (+54/−52).

Key words: Lanthanum, Tetrelides, Stannides, Germanides, Band Structure Calculation