substance: transition metal-$(V)_3$ compounds
property: crystal structure, chemical bond of transition element tripnictides

The semiconducting transition-element tripnictides all crystallize in the cubic skutterudite structure (see document), which is related to the pyrite type. In this polyanion structure the cations have again a distorted octahedral coordination (T – 6X). Each octahedron shares corners with six neighboring octahedra. Layers of octahedra are similar to those in pyrite, however, the octahedra are tilted in a different way so that rectangular (nearly square) anion rings are formed. Each anion is bonded to two anions and two cations which form the corners of a strongly distorted tetrahedron. In skutterudite-type pnictides, semiconductivity is possible only with d^6 cations of an average oxidation number three. Arsenides appear to be slightly anion-deficient [62R]. Probably all skutterudite-type representatives form peritectically [60Z, 61K]. Peritectic temperatures are 859°C for $CoSb_3$ [56D, 58D, 60Z] and ≈ 900°C for $RhSb_3$ and $IrSb_3$ [60Z].

Doping of the skutterudite pnictides is possible with cations of the iron and nickel group. The anion can be partially substituted by group IV and group VI neighbors of the Periodic System.

No measurable homogeneity range was found for $Co_{1-x}M_xSb_3$ and $CoSb_{3-y}X_y$ with M = Cu, Zn, Al, Ti and X = Si, Ge, Pb, Se [59D] and for $Rh_{1-x}Ru_xAs_3$, $Rh_{1-x}Ag_xAs_3$ and $Ir_{1-x}Os_xAs_3$ at 750°C [66B]. Isoelectronic substitutions, however, are possible. Thus, semiconducting ternary skutterudites (with rhombohedral superstructure due to anion ordering) are known: $Co_2Ge_3S_3$, $Co_2Ge_3Se_3$ [77K], $Ir_2Ge_3S_3$, $Ir_2Ge_3Se_3$, $Ir_2Sn_3S_3$, $Rh_2Ge_3S_3$ [78L].

Isoelectronic substitution is possible also for the cation. Whereas the antimonide $Fe_{0.5}Ni_{0.5}Sb_3$ [70B] is stoichiometric and thus truly isoelectronic, the corresponding arsenide is found to exist within a broad solubility range $Fe_{1-x}Ni_xAs_3$, x = 0.25...0.46 but apparently not with the isoelectronic composition [62P].

The skutterudite structure contains two large voids (at the positions 2(a) of the cubic unit cell), which can be filled with additional cations. A large family of electron-deficient ternaries LnT_4X_{12} exists where Ln is one of the larger rare-earth elements La, Ce, ...; T = Fe, Ru, Os, and X = P, As, Sb [77J, 80B1, 80B2]. Since the iron-group cation is divalent, semiconductivity could be expected only with tetravalent thorium or cerium, as met in $ThFe_4P_{12}$, $CeFe_4P_{12}$ and $CeFe_4As_{12}$ [80B1, 80B3]. However, an intermediate valence was claimed not only for Ce in $CeFe_4P_{12}$ but also for Th in $ThRu_4P_{12}$ [80B3], though finally $CeFe_4P_{12}$ was found to be semiconducting [82G]. $CeFe_4Sb_{12}$, on the other hand, was reported to behave as a metal [80B2].

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