Neue gemischte Zinn-reiche Erdalkalimetall-Stannide – Synthese, Strukturchemie und chemische Bindung

New Mixed Tin-rich Alkaline Earth Stannides – Synthesis, Structural Chemistry and Chemical Bonding

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Ternary mixed Ca/Ba-Sr pentastannides $A^{II}Sn_5$ (A^{II} = Ca, Sr, Ba) have been synthesized from stoichiometric mixtures of the elements or from tin-rich melts. The crystal structures of two new compounds of overall composition ASn_5 (A = Sr, Ba) were determined by means of single-crystal X-ray data. The structures of both $Sr_{0.94}Ba_{0.06}Sn_5$ (monoclinic, space group *C2/m*, a = 1762.8(11), b = 704.1(3), c = 1986(2) pm, β = 100.31(6)°, Z = 14, $R1$ = 0.0996) and $Sr_{0.89}Ba_{0.11}Sn_5$ (orthorhombic, space group *Cmcm*, a = 708.1(2), b = 1770.4(8), c = 2781.6(11) pm, Z = 20 , $R1$ = 0.0821) are closely related and can be described by different stacking sequences of comparable nets. They both resemble the structural features of the tristannides $A^{II}Sn_3$ in forming dimers and trimers of face-sharing Sn_6-octahedra, which are further connected *via* common corners. According to the higher tin content, the rods formed of the octahedra are interspersed by additional Sn atoms, which themselves show a bonding situation resembling the structure of elementary tin. The complex tin network formed by the strong Sn-Sn bonds alone can be regarded as a cutout of the hexagonal diamond structure. In this view, the similarities of the title compounds to the known binary stannides $BaSn_5$ and $SrSn_4$ become apparent. The phase widths of the latter have been investigated and shown to reach up to $Sr_{0.37}Ba_{0.63}Sn_5$ ($BaSn_5$ type, hexagonal, space group *P6/mmm*, a = 536.8(2), c = 695.2(3) pm, $R1$ = 0.0312) and $Sr_{0.79}Ca_{0.21}Sn_4$ ($SrSn_4$ type, orthorhombic, space group *Cmcm*, a = 461.7(3), b = 1714.1(14), c = 706.7(4) pm, Z = 4, $R1$ = 0.0861), respectively. The total density of states calculated for the orthorhombic pentastannide within the FP-LAPW DFT band structure approach shows a broad minimum at the Fermi level, which can be explained using the Zintl and the Wade/Jemmis electron counting rules.

Key words: Stannides, Strontium, Crystal Structure, Band Structure Calculation