

# Gemischte Plumbide (Ca/Sr)<sub>x</sub>Ba<sub>1-x</sub>Pb<sub>3</sub>. Strukturchemie und chemische Bindung

Mixed Plumbides (Ca/Sr)<sub>x</sub>Ba<sub>1-x</sub>Pb<sub>3</sub>. Structural Chemistry and Chemical Bonding

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Ternary mixed Ca/Sr-Ba triplumbides of overall composition A<sup>II</sup>Pb<sub>3</sub> were synthesized from stoichiometric mixtures of the elements. The structures of the compounds have been determined by means of single crystal X-ray data. All structures exhibit close-packed ordered APb<sub>3</sub> layers containing Pb Kagomé nets, which are stacked in different orientations. Depending on the stacking sequences, the resulting lead polyanion resembles the oxygen nets of the hexagonal (face sharing octahedra, *h* stacking, Ni<sub>3</sub>Sn-type structure) or the cubic perovskites (corner sharing octahedra, *c* stacking, Cu<sub>3</sub>Au-type structure). The known binary compound BaPb<sub>3</sub>, the structure of which has been re-determined from single crystal data (trigonal, space group  $R\bar{3}m$ ,  $a = 729.06(2)$ ,  $c = 2564.43(10)$  pm,  $Z = 9$ ,  $R1 = 0.0353$ ), shows a (*hcc*)<sub>3</sub> stacking (TaCo<sub>3</sub>-type structure). A small partial substitution of barium against calcium (Ca<sub>0.03</sub>Ba<sub>0.97</sub>Pb<sub>3</sub>: trigonal, space group  $R\bar{3}m$ ,  $a = 726.0(2)$ ,  $c = 3443(2)$  pm,  $Z = 12$ ,  $R1 = 0.0542$ ) or strontium (Sr<sub>0.11</sub>Ba<sub>0.89</sub>Pb<sub>3</sub>:  $a = 727.3(2)$ ,  $c = 3421(2)$  pm,  $Z = 12$ ,  $R1 = 0.0424$ ) causes a structural change to the HT-PuGa<sub>3</sub> structure type with a (*hcc*)<sub>3</sub> stacking sequence. At an approximate 1 : 1 ratio (35 to 53 % Sr) of strontium and barium (Sr<sub>0.56</sub>Ba<sub>0.44</sub>Pb<sub>3</sub>: trigonal, space group  $P6_3/mnc$ ,  $a = 715.82(2)$ ,  $c = 1717.91(7)$  pm,  $Z = 6$ ,  $R1 = 0.0309$ ) the PuAl<sub>3</sub> structure type [(*hcc*)<sub>2</sub>-stacking] has a distinct homogeneity range. The series is terminated with the pure *c* stacking of SrPb<sub>3</sub> and CaPb<sub>3</sub>. As already noted from the above series, the stacking of the close-packed layers is influenced by the ratio of the atomic radii of the contributing elements. The electronic stability ranges, which are discussed on the basis of the results of FP-LAPW band structure calculations and in comparison to further compounds known from the literature, can be explained using Zintl/Wade rules. Still, due to the presence of only partially occupied steep Pb-*p* bands of  $\sigma$  bonding characteristic, the compounds are metals exhibiting pseudo band gaps at or near the Fermi level. Thus this structure family represents an instructive case of transition from polar ionic/covalent towards (inter)metallic chemistry.

**Key words:** Plumbides, Barium, Crystal Structure, Band Structure Calculation