$Ba_5Al_2Ge_7$ und $Ba_7Al_4Ge_9$: Zwei neue intermetallische Phasen mit ungewöhnlichen Al-Ge-Anionen

$Ba_5Al_2Ge_7$ and $Ba_7Al_4Ge_9$:
Two New Intermetallic Phases with Unusual Al-Ge Anions

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In the ternary system Ba-Al-Ge new intermetallic compounds which are lying on or close to the binary section $BaAl_2$ – $BaGe_2$ were synthesized from the elements and characterized on the basis of X-ray single crystal data. The Al-content x in the compounds $BaAl_xGe_{2-x}$ forming the AlB_2 structure type ranges from $x = 1.4$ [$BaAl_{1.4}Ge_{0.6}$: space group $P6/mmm$, $a = 443.5(1)$, $c = 512.4(1)$ pm, $Z = 1$, $R1 = 0.0222$] to the stoichiometric ordered compound BaAlGe [space group $P\bar{6}m2$, $a = 434.9(1)$, $c = 513.6$ pm, $Z = 1$, $R1 = 0.0252$]. In the two new Ge-rich barium intermetallics $Ba_5Al_2Ge_7$ [space group $C2/m$, $a = 859.8(4)$, $b = 1031.5(4)$, $c = 1847.8(6)$ pm, $\beta = 103.23(3)^\circ$, $Z = 4$, $R1 = 0.0553$] and $Ba_7Al_4Ge_9$ [space group $Fmm2$, $a = 1032.7(5)$, $b = 2559(2)$, $c = 862.1(4)$ pm, $Z = 4$, $R1 = 0.1197$] complex Al/Ge polyanions are present, which consist of (1) Al/Ge-ribbons of condensed planar six-membered rings comparable to the anions in $Ba_3Al_2Ge_2$, and (2) $[Ge/Al]_5$ clusters comparable to the anions in the tetrelides Ba_3M_5. The building units (1) and (2) are connected *via* Al-Ge bonds to form complex ribbons in the case of $Ba_5Al_2Ge_7$ and sheets in the case of $Ba_7Al_4Ge_9$. The electron count in the two compounds supports an interpretation of the structures according to the Zintl concept and the Wades rules. The small formal electron excess, caused by the incomplete transfer of charge from Ba towards the Al/Ge polyanions, decreases with the Ge content of the compound.

Key words: Barium, Aluminium, Germanium, Zintl Phases, Cluster Compounds