

New Chalcogenogermanates with Adamantane Type Complex Anions: Preparation and Crystal Structures of $\text{K}_4\text{Ge}_4\text{S}_{10}$; $\text{Rb}_4\text{Ge}_4\text{S}_{10}$, $\text{Rb}_4\text{Ge}_4\text{Se}_{10}$, and $\text{Cs}_4\text{Ge}_4\text{Se}_{10}$

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Crystal Structure, Complex Chalcogenides, Alkali Thiogermanate(IV),
Alkali Selenogermanate(IV)

The title compounds were obtained by reacting stoichiometric quantities of the corresponding dialkalimonochalcogenide, germanium powder and chalcogen at 1073 K. The four compounds are isostructural, crystallizing in space group $C2/c$, $Z = 4$ with $\text{K}_4\text{Ge}_4\text{S}_{10}$: $a = 15.161(3)$, $b = 15.198(2)$, $c = 8.760(2)$ Å, $\beta = 105.36(3)^\circ$, $\text{Rb}_4\text{Ge}_4\text{S}_{10}$: $a = 15.282(7)$, $b = 15.341(7)$, $c = 9.061(4)$ Å, $\beta = 106.10(3)^\circ$; $\text{Rb}_4\text{Ge}_4\text{Se}_{10}$: $a = 16.095(9)$, $b = 16.09(1)$, $c = 9.390(7)$ Å, $\beta = 105.79(2)^\circ$ and $\text{Cs}_4\text{Ge}_4\text{Se}_{10}$: $a = 16.348(9)$, $b = 16.49(1)$, $c = 9.771(3)$ Å, $\beta = 107.10(3)^\circ$. Their crystal structures were solved and refined from single crystal diffractometer data ($\text{MoK}\alpha$ radiation) obtained at 294 K. They are characterized by the formation of discrete adamantane-like complex anions $[\text{Ge}_4\text{Q}_{10}]^{4-}$ which are arranged in slabs parallel to (010). Mean Ge-S bond lengths are 2.202 Å for $\text{K}_4\text{Ge}_4\text{S}_{10}$ and 2.186 Å for $\text{Rb}_4\text{Ge}_4\text{S}_{10}$ while the mean Ge-Se bond length in both selenides amounts to 2.332(3) Å. Terminal and bridging Ge-Q bonds differ by at least 0.1 Å. The atomic arrangement corresponds to that of $\text{Tl}_4\text{Ge}_4\text{S}_{10}$.