

Münzmetall-Lanthanid-Chalkogenide: II. Kupfer(I)-Lanthanid(III)-Sulfide der Zusammensetzung CuMS_2 ($M = \text{Dy} - \text{Lu}$) im orthorhombischen B-Typ

Coinage Metal Lanthanide Chalcogenides: II. Copper(I) Lanthanide(III) Sulfides of the Composition CuMS_2 ($M = \text{Dy} - \text{Lu}$) with the Orthorhombic B-Type Structure

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Z. Naturforsch. **2007**, 62b, 15 – 22; eingegangen am 10. August 2006

Single crystals of the ternary copper(I) lanthanide(III) sulfides with the composition CuMS_2 ($M = \text{Dy} - \text{Lu}$) are formed within seven days at 750 °C by oxidation of elemental copper and lanthanide metal with sulfur (molar ratio: 1 : 1 : 2, evacuated silica tubes) in equimolar quantities of CsCl, CsBr or CsI as fluxing agents. The CuYS_2 -type crystal structures (orthorhombic, *Pnma*, $Z = 4$; e. g. CuDyS_2 : $a = 1342.51(9)$, $b = 397.96(3)$, $c = 627.43(5)$ pm and CuLuS_2 : $a = 1315.06(9)$, $b = 391.04(3)$, $c = 624.18(5)$ pm) exhibit chains of *cis* edge-linked $[\text{CuS}_4]^{7-}$ tetrahedra with the composition ${}^\infty_1\{[\text{Cu}(\text{S}1)_{3/3}(\text{S}2)_{1/1}]^{3-}\}$ which run parallel to [010] and show hexagonal rod packing. Charge compensation and three-dimensional interconnection of these anionic strands occur *via* octahedrally coordinated M^{3+} cations surrounded by six S^{2-} anions. These $[\text{MS}_6]^{9-}$ octahedra share vertices and edges to form a three-dimensional network ${}^\infty_3\{[M(\text{S}1)_{3/3}(\text{S}2)_{3/3}]^{-}\}$ with the ramsdellite-type topology of $\gamma\text{-MnO}_2$. The metal sulfur distances within the $[\text{MS}_6]$ polyhedra are very similar ($M\text{-S}$: 263 – 279 pm), whereas those within the $[\text{CuS}_4]$ units cover the ranges 227 – 230 (Cu–S2) and 231 – 233 (Cu–S1) as well as 250 – 252 pm (Cu–S1', $2\times$). The present work is the first comprehensive X-ray single crystal diffraction study of the complete isotypic B-type series CuMS_2 ($M = \text{Dy} - \text{Lu}$).

Key words: Sulfides, Lanthanides, Copper, Crystal Structures