Münzmetall-Lanthanid-Chalkogenide: I. Kupfer(I)-Lanthanid(III)-Sulfide der Zusammensetzung CuMS$_2$ (M = La – Nd, Sm, Gd, Tb) im monoklinen A-Typ

Coinage Metal Lanthanide Chalcogenides: I. Copper(I) Lanthanide(III) Sulfides of the Composition CuMS$_2$ (M = La – Nd, Sm, Gd, Tb) with the Monoclinic A-Type Structure

Sabine Strobel, Petra Lauxmann und Thomas Schleid

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart

Sonderdruckanforderungen an Prof. Dr. Thomas Schleid. Fax: +49(0)711/685-4241.
E-mail: schleid@iac.uni-stuttgart.de

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Single crystals of the ternary copper(I) lanthanide(III) sulfides with the composition CuMS$_2$ (M = La – Nd, Sm, Gd, Tb) form within seven days at 800 °C by oxidation of elemental copper and lanthanide metal with sulfur (molar ratio: 1 : 1 : 2) in evacuated silica tubes when equimolar quantitites of CsCl are present as flux. The crystal structures (monoclinic, $P2_1/c$, $Z = 4$; *e. g.* CuLaS$_2$: $a = 662.04(6)$, $b = 730.89(6)$, $c = 692.73(6)$ pm, $\beta = 98.741(7)^\circ$ and CuTbS$_2$: $a = 639.13(6)$, $b = 700.02(6)$, $c = 670.46(6)$ pm, $\beta = 98.214(7)^\circ$) exhibit corrugated layers $^2_\infty\{[\mathrm{Cu(S1)}_{3/3}\mathrm{(S2)}_{1/1}]^{3-}\}$ parallel to (100) which consist of vertex-linked pairs of $[CuS_4]^{7-}$ tetrahedra sharing a common edge ($[Cu_2S_6]^{10-}$). Their three-dimensional cross-linkage is achieved by M^{3+} cations in monocapped trigonal prismatic coordination of seven S^{2-} anions. The metal sulfur distances in the $[CuS_4]^{7-}$ units cover with 230 – 233 (Cu–S2) and 231 – 238 (Cu–S1) as well as 241 – 248 (Cu–S1') and 245 – 251 pm (Cu–S1") a rather broad range, whereas those within the $[MS_7]^{11-}$ polyhedra lie relatively closer together (M–S: 276 – 307 pm). The present work is the first comprehensive account of the knowledge acquired from X-ray single-crystal diffraction data for the whole isotypic series CuMS$_2$ (M = La – Nd, Sm, Gd, Tb).

Key words: Sulfides, Lanthanides, Copper, Crystal Structures