

Nitridsulfidhalogenide der leichten Lanthanide vom Typ $M_6N_3S_4X$ ($M = La - Nd$; $X = Cl, Br$) mit ausgeordneten Sulfid- und Halogenid-Lagen

Nitride Sulfide Halides of the Light Lanthanides with the Formula Type $M_6N_3S_4X$
($M = La - Nd$; $X = Cl, Br$) with Ordered Sulfide and Halide Positions

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The oxidation of the light lanthanides ($M = La - Nd$) with sulfur and NaN_3 in the presence of the tribromides MBr_3 yields bromine-poor nitride sulfide bromides with the composition $M_6N_3S_4Br$ when appropriate molar ratios of the reactants are used. Additional $NaBr$ as a flux secures complete and fast reactions (7 d) at $850\text{ }^\circ\text{C}$ in evacuated silica tubes as well as single-crystals of the pure phase (brownish needles). The orthorhombic crystal structure ($Pnma$, $Z = 4$) was determined from single crystal X-ray data for $La_6N_3S_4Br$ ($a = 1159.23(9)$, $b = 410.85(3)$, $c = 2765.6(2)$ pm), $Ce_6N_3S_4Br$ ($a = 1152.31(9)$, $b = 407.52(3)$, $c = 2747.4(2)$ pm), $Pr_6N_3S_4Br$ ($a = 1145.42(9)$, $b = 404.21(3)$, $c = 2729.3(2)$ pm), and $Nd_6N_3S_4Br$ ($a = 1138.59(9)$, $b = 400.94(3)$, $c = 2711.3(2)$ pm). Six crystallographically different M^{3+} cations are present, two of them ($M1$ and $M2$) build up chain I ($\frac{1}{\infty}\{[NM_2]^{3+}\}$) by *cis*-edge connection of $[NM_4]$ tetrahedra. The four remainders ($M3 - M6$) arrange as pairs $[N_2M_6]$ of edge-shared $[NM_4]$ units which are further connected *via* four vertices to form a double chain (chain II = $\frac{1}{\infty}\{[N_2M_4]^{6+}\}$). Bundled along $[010]$ like a closest packing of rods, both types of chains are commensurate in translation and held together by one Br^- and four S^{2-} anions which, in contrast to an earlier work on the *pseudo*-isotypic chloride analogues $M_6N_3S_4Cl$ ($M = La - Nd$), are perfectly ordered.