Die Lanthanid(III)-*ortho*-Thiophosphate(V) vom Typ $M[PS_4]$ (M = La–Nd, Sm, Gd–Er): Synthese, Kristallstruktur und ^{31}P-NMR-Untersuchungen

The $M[PS_4]$-Type Lanthanide(III) *ortho*-Thiophosphates(V) (M = La–Nd, Sm, Gd–Er): Synthesis, Crystal Structure, and ^{31}P NMR Investigations

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Single crystals of the lanthanide(III) thiophosphates(V) with the composition $M[PS_4]$ (M = La–Nd, Sm, Gd–Er) are formed within seven days at 950 °C by oxidation of the lanthanide metals and red phosphorus with sulfur (molar ratio: 1 : 1 : 4) in evacuated silica tubes without using any flux to avoid the entrapment of *e. g.* alkali metal cations. Their crystal structure (tetragonal, $I4_1/acd$, $Z = 16$; *e. g.* $La[PS_4]$: $a = 1098{,}97(5)$; $c = 1953{,}26(9)$ pm and $Er[PS_4]$: $a = 1062{,}41(5)$; $c = 1892{,}38(9)$ pm for the borderline representatives discussed here) is built up by a distorted cubic closest packing of discrete $[PS_4]^{3-}$ tetrahedra ($d(P^{5+}–S^{2-}) = 203 – 204$ pm; $\sphericalangle(S–P–S) = 107 – 116°$) where the M^{3+} cations are situated in one half of the tetrahedral interstices, the same way as S^{2-} in the Pt^{2+} arrangement of the *cooperite*-type PtS structure. Therefore an eightfold sulfur coordination for both crystallographically independent M^{3+} cations results in the shape of a trigonal dodecahedron. The ^{31}P-MAS-NMR spectra of $La[PS_4]$, $Nd[PS_4]$, $Gd[PS_4]$, and $Er[PS_4]$ are reported and discussed.

Key words: Lanthanides, Thiophosphates, Crystal Structures, ^{31}P NMR Investigations