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

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

Theresa Komm, Dietrich Gudat und Thomas Schleid

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

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


Professor Wolfgang Jeitschko zum 70. Geburtstag gewidmet

Single crystals of the lanthanide(III) thiophosphates(V) with the composition $M[PS_4]$ ($M = \text{La–Nd, Sm, Gd–Er}$) 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 ($d(\text{P}^5+–\text{S}^2-) = 203 – 204$ pm; $\angle(\text{S}–\text{P}–\text{S}) = 107 – 116^\circ$) where the $M^{3+}$ cations are situated in one half of the tetrahedral interstices, the same way as $\text{S}^2-$ 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