

Oxidfluoridsulfide der Lanthanoide vom Formeltyp M_3OF_5S

($M = \text{Nd, Sm, Gd-Ho}$)

Oxide Fluoride Sulfides of the Lanthanoids with the Formula M_3OF_5S ($M = \text{Nd, Sm, Gd-Ho}$)

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First attempts to synthesize a lanthanoid(III) oxide fluoride sulfide were successful by reacting DyF_3 and Dy_2O_3 with dysprosium and sulfur in a 2 : 5 : 1 : 3 molar ratio at 850 °C in tightly sealed tantalum ampoules. In analogy to the dysprosium compound $\text{Dy}_3\text{OF}_5\text{S}$, the other representatives of the $M_3\text{OF}_5\text{S}$ series with $M = \text{Nd, Sm, Gd-Ho}$ could be prepared as well. Almost phase-pure samples were obtained under similar flux-assisted (NaCl) conditions according to $2M + 5\text{MF}_3 + M_2\text{O}_3 + 3\text{S} \rightarrow 3M_3\text{OF}_5\text{S}$. In the hexagonal crystal structure (space group: $P6_3/m$; $a \approx 961-939$ pm, $c \approx 378-367$ pm; $c/a \approx 0.39$, $V_m \approx 91-84$ cm³ mol⁻¹, $Z = 2$), the M^{3+} cations reside in ninefold anionic coordination realized as tricapped trigonal prisms formed by seven light (O^{2-}/F^-) and two heavier S^{2-} anions. One light-anion position exhibits the exclusive character of F^- in trigonal non-planar coordination (CN = 3), while the other position with a tetrahedral cationic environment (CN = 4) is mixed occupied by F^- and O^{2-} in a 2 : 1 ratio. The S^{2-} anions are coordinated in a trigonal prismatic way by six M^{3+} cations. From the data of single-crystal X-ray structure analyses, no indication of any ordering for the O^{2-} and F^- anions could be obtained, but bond-valence and MAPLE calculations confirmed the results of electron-beam microanalyses carried out earlier to reveal ordered models for $\text{Dy}_3\text{OF}_5\text{S}$.

Key words: Lanthanides, Oxide Fluoride Sulfides, Crystal Structures