Die Selten-Erd-Metall(III)-Fluorid-Oxoselenate(IV) MF[SeO_3] (M = Y, Ho – Lu) im YF[SeO_3]-Typ

The Rare-Earth Metal(III) Fluoride Oxoselenates(IV) MF[SeO_3] (M = Y, Ho–Lu) with YF[SeO_3]-type Structure

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YF[SeO_3]-type rare-earth metal(III) fluoride oxoselenates(IV) MF[SeO_3] (M = Y, Ho–Lu) crystallize monoclinically in space group $P2_1/c$ (no. 14) with $Z = 4$. Obeying the lanthanoid contraction, the lattice parameters decrease successively from a = 657.65(7), b = 689.71(7), c = 717.28(7) pm and β = 99.036(5)° for YF[SeO_3] at 298 K to a = 648.39(6), b = 681.28(7), c = 705.81(7) pm and β = 98.657(5)° for LuF[SeO_3] at 100 K (LT-LuF[SeO_3], LT ≡ **L**ow **T**emperature). The M^{3+} cations are occupying the general site 4*e*. Contrary to the triclinic structure of RT-LuF[SeO_3] (RT ≡ **R**oom **T**emperature; CN(Lu^{3+}) = 7) the higher coordination number *eight* is achieved for the M^{3+} cations in all YF[SeO_3]-type compounds. This results in $[MO_6F_2]^{11-}$ polyhedra (d(M–O) = 228 – 243/225 – 239 *plus* 263/258 pm, d(M–F) = 219/216 pm, M = Y/Lu), which are connected *via* common O···O edges to form infinite chains ${}^1_\infty\{[MO^e_{4/2}O^t_{2/1}F^t_{2/1}]^{7-}\}$ (e ≡ edge-sharing, t ≡ terminal) running along [010]. Neighboring chains share common O3···O3 and O3···F edges generating ${}^2_\infty\{[M(O3)_{3/3}(O2)_{2/2}(O1)_{1/1}F_{2/2}]^{4-}\}$ sheets parallel to the (100) plane. Finally, these ${}^2_\infty\{[MO_3F]^{4-}\}$ sheets are interconnected by Se^{4+} cations, which appear in isolated ψ^1-tetrahedral $[SeO_3]^{2-}$ anions (d(Se–O) = 167 – 175 pm). For the synthesis of the YF[SeO_3]-type rare-earth metal(III) fluoride oxoselenates(IV) MF[SeO_3] (M = Y, Ho–Lu), the rare-earth metal sesquioxides (M_2O_3) and trifluorides (MF_3), and selenium dioxide (SeO_2) in molar ratios of 1 : 1 : 3 with the fluxing agent CsBr were reacted within five days at 700 – 750 °C in evacuated graphitized silica ampoules.

Key words: Rare-Earth Metals, Fluorides, Oxoselenates(IV), Crystal Structures