MS15-1-2 $Sm_7F_{12}Cl_2$: Synthesis and Crystal Structure of a New Fluoride-Rich Samarium(II) Fluoride Chloride #MS15-1-2

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Abstract
Red rod-shaped single crystals of $Sm_7F_{12}Cl_2$ (CSD-2126941) with a length up to 0.3 mm were obtained as a by-product in an experiment to obtain SmF_2 [1–4] from a NaCl flux. SmF_2 occurs as red plates in the CaF_2-type structure (cubic, $Fm\bar{3}m$, a = 580.31(4) pm, d(Sm−F) = 2501 pm, 8×) [4]. Both kinds of single crystals emerged after heating up a mixture of Sm, SmF_3 and NaCl (as flux) in a sealed niobium capsule to 850 °C and cooling down the product with 5 °C/h after four days. $Sm_7F_{12}Cl_2$ crystallizes in the $Ba_7F_{12}Cl_2$-type structure [5] with a = 1004.52(7) pm, c = 394.75(3) pm and Z = 1 (space group: $P\bar{6}$) analogous to $Eu_7F_{12}Cl_2$ [6]. For H^- instead of F^- anions, this structure is also known for $Sr_7H_{12}Cl_2$ [7] and $Ca_7H_{12}Cl_2$ [8]. There are three crystallographically independent Sm^{2+} cations, all coordinated by nine anions in the shape of tricapped trigonal prisms. While $(Sm1)^{2+}$ only enjoys coordination from F^- anions (d(Sm1)−F) = 240 – 275 pm), $(Sm2)^{2+}$ and $(Sm3)^{2+}$ carry seven F^- anions at distances between 246 and 278 pm and two Cl^- anions with distances of about 314 pm as ligands. $(F1)^-$, $(F2)^-$ and $(F3)^-$ are coordinated tetrahedrally, while $(F4)^-$ has a square pyramidal Sm^{2+} environment. The coordination spheres of both Cl^- anions consist of six Sm^{2+} cations in shape of trigonal prisms. The atomic parameters are given in Table 1 and the unit cell of $Sm_7F_{12}Cl_2$ is shown in Figure 1 as viewed along [001]. A second samarium(II) fluoride chloride with the formula SmFCl adopts the PbFCl-type structure (tetragonal, a = 413.59(5) pm, c = 699.34(11) pm) [4] exhibiting four Sm−F distances of 252 pm and five Sm−Cl distances of 307 pm (1×) and 311 pm (4×) [4] in capped square antiprismatic coordination sphere.

Atomic coordinates, Wyckoff positions and equivalent isotropic displacement parameters for hexagonal $Sm_7F_{12}Cl_2$.

Atom	**Site**	***x*/*a***	***y*/*b***	***z*/*c***	U_{eq} / pm^2
Sm1	1*a*	0	0	0	232(4)
Sm2	3*j*	0.40813(12)	0.11180(12)	0	121(3)
Sm3	3*k*	0.28971(11)	0.40317(11)	$^1/_2$	92(2)
F1	3*j*	0.1226(14)	0.2757(14)	0	179(26)
F2	3*j*	0.4262(16)	0.3659(16)	0	233(37)
F3	3*k*	0.0501(14)	0.4375(14)	$^1/_2$	110(27)
F4	3*k*	0.2195(15)	0.1250(15)	$^1/_2$	211(29)
Cl1	1*c*	$^1/_3$	$^2/_3$	0	193(19)
Cl2	1*f*	$^2/_3$	$^1/_3$	$^1/_2$	110(17)

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Extended unit cell of $Sm_7F_{12}Cl_2$ viewed along [001]