

5 Summary and Outlook

5.1 Results

This work starts with a simple synthesis procedure for the rare-earth fluoride sulfides (MFS) of the tetragonal A-type. The compounds are obtained quantitatively by reacting a mixture of a lanthanide metal (M), lanthanide trifluoride (MF_3) and elemental sulfur (S) in an NaCl-flux at 850°C . In addition to the rare-earth(III) fluoride sulfides, MFS compounds reached even the composition $\text{M}_3\text{F}_4\text{S}_2$ for samarium and europium. Owing to their appearance and the results obtained from temperature dependent magnetic susceptibility measurements and temperature dependent ^{151}Eu -Mössbauer spectroscopy, the investigated compounds have to be interpreted as mixed valent ($\text{M}^{2+}/\text{M}^{3+}$). An oxygen contamination during the synthesis of A-DyFS lead to the first hexagonal rare-earth(III) oxyfluoride sulfide ($\text{Dy}_3\text{OF}_5\text{S}$). On adding more dysprosium sesquioxide (Dy_2O_3) to a mixture of $\text{MF}_3 : \text{M} : \text{S}$ almost single phase crystals were got. Further compounds with the same sum formula type $\text{M}_3\text{OF}_5\text{S}$ ($\text{M} = \text{Nd}, \text{Sm}$ and $\text{Gd} - \text{Ho}$) have been synthesized and characterized by X-ray diffraction measurements. The lighter rare-earth elements lanthanum to neodymium and samarium form a closely related hexagonal structure type with the sum formula $\text{M}_6\text{O}_2\text{F}_8\text{S}_3$ ($\text{M} = \text{La} - \text{Nd}, \text{Sm}$). When compared to this, the rare-earth elements (Y, Ho and Yb) with smaller ionic radius show a stacked "pseudo-tetragonal" crystal structure with the sum formula $\text{M}_3\text{OF}_3\text{S}_2$ ($\text{M} = \text{Y}, \text{Ho}$ and Tm) under chosen reaction conditions. Till now the ordering of the "light anions" fluoride (F^-) and oxide (O^{2-}) in the investigated rare-earth oxyfluoride sulfides has not been absolutely defined by the single crystal X-ray diffraction measurements. The different coordination of the "light anions" and MAPLE calculations theoretically indicate special theoretical crystal structure models, too, but do not give an established relation to the real crystal structures. Experiments to get the analogue selenide compounds lead to isostructural compounds $\text{M}_6\text{O}_2\text{F}_8\text{Se}_3$ ($\text{M} = \text{La}, \text{Pr}$) as well as new compounds with different sum formulas and different crystal structures. It has been shown that by the formal derivatization of the chalcogenide ions a wide range of different phases in the compound system can be attained. The following new compounds MFSe ($\text{M} = \text{La}, \text{Pr}$), $\text{M}_2\text{F}_4\text{Se}$ ($\text{M} = \text{Pr}, \text{Nd}$), A- $\text{La}_2\text{OF}_2\text{Se}$, $\text{M}_6\text{O}_3\text{F}_8\text{Se}_3$ ($\text{M} =$

La, Nd) and $B-M_2OF_2Se$ ($M = Gd, Ho$) crystallized out of a NaCl flux at $850^\circ C$. Literature studies lead to the syntheses of compounds which contain a rare-earth element, fluorine and chalcogene as well as a transition metal. In this work the tantalum compounds $M_3F_2Se_2TaO_4$ ($M = La, Nd$) (isotypical to the accidentally obtained niobium compound $La_3F_2Se_2NbO_4$) and $La_2FSeNbO_4$ have been synthesized and characterized. In addition to these, new copper(I) rare-earth(II) fluoride sulfide and selenide compounds ($CuEuFS$ and $CuSmFSe$) have been investigated.

5.1.1 Fluoride Sulfides

5.1.1.1 Fluoride Sulfides MFS of the A-, B- and C-Type

The reaction of elemental rare-earth metals (M) with sulfur (S) and the corresponding trifluoride (MF₃) in gastight sealed tantalum ampoules (850°C, 7 d) with 2 : 3 : 1 molar ratios of the educts (M : S : MF₃), pure and single-phase fluoride sulfides of the composition MFS are obtained. In the A-MFS crystal structure of the PbFCl-type, the M³⁺ cations are present in a capped square antiprismatic coordination of four F⁻ and five S²⁻ anions, which again are surrounded by four and five cations, respectively, in tetrahedral (F⁻) or square pyramidal (S²⁻) manner. Contrary to this, the closely related crystal structures of B-MFS and C-MFS each exhibit two crystallographically different M³⁺ cations. In both cases, M1 is surrounded trigonal antiprismatic by six S²⁻, whereas M2 is hexagonal-bipyramidally coordinated by eight anions (six F⁻ within the equatorial plane, two S²⁻ as apical ligands) altogether. The anions themselves reside in a trigonal planar (F⁻) or distorted tetrahedral (S²⁻) coordination of three and four cations, respectively. Regarding both the structures as built up by triple- ($\infty^2 \{((S^{2-})-(M^{3+})-(S^{2-}))\}^-$) and single-layer slabs ($\infty^2 \{(M^{3+})(F^-)_2\}^+$) alternately stacked parallel (001), the B-type and the C-type structures only differ in their stacking sequence: In the B type a **(2x2)H** structure is present, while the C type on the other hand shows a **(3x2)R** arrangement, according to the *Ramsdell* nomenclature for layered structures.

A-MFS: tetragonal, P4/nmm (No. 129)

	a / pm	c / pm	c / a
CeFS	400.13(3)	696.20(5)	1.740
PrFS	396.27(3)	692.73(5)	1.748
NdFS	393.89(3)	691.58(5)	1.756
SmFS	388.36(3)	687.95(5)	1.771
GdFS	383.45(3)	685.18(5)	1.787
TbFS	381.02(3)	683.86(5)	1.795
DyFS	378.54(2)	682.67(2)	1.803
HoFS	376.48(3)	681.92(5)	1.811
ErFS	374.61(3)	681.34(5)	1.819

5.1.1.2 Mixed-Valent Fluoride Sulfides $M_3F_4S_2$

The mixed-valent rare-earth fluoride sulfides are obtained by the reaction of rare-earth metal (M), elemental sulfur (S) and rare-earth trifluoride (MF_3) in a molar ratio of 5 : 6 : 4 after seven days at 850°C in silica-jacketed gastight-sealed, arc-welded tantalum-ampoules (Eu: platinum-ampoules). The almost single-phase product turns single-crystalline, forming shiny black plates with square cross section on adding equimolar amounts of NaCl as fluxing agent. Its crystal structure can be described as an intergrowth layered structure, in which one layer of CaF_2 -type EuF_2 is followed by two layers of $PbFCl$ -type $EuFS$ parallel (001). Temperature dependent magnetic susceptibility measurements of $Eu_3F_4S_2$ show Curie-Weiss behaviour with an experimental magnetic moment of 8.19(5) μ_B /formula unit and a paramagnetic Curie temperature of 0.3(2) K. No magnetic ordering is observed down to 4.2 K. In accordance with an ionic formula splitting like $Eu^{II}(Eu^{III})_2F_4S_2$ only one third of the europium atoms in $Eu_3F_4S_2$ carry permanent magnetic moments. ^{151}Eu -Mössbauer spectroscopic experiments at 4.2 K show one signal at an isomer shift of $-12.4(1)$ mm/s and a second one at 0.42(4) mm/s. These signals occur in a ratio of 1 : 2 and correspond to Eu^{2+} and Eu^{3+} , respectively. No change in the Eu^{2+}/Eu^{3+} fraction is observed. According to these data $Eu_3F_4S_2$ may be classified as a static mixed-valent system.

$M_3F_4S_2$: tetragonal, I4/mmm (No. 139)			
	a / pm	c / pm	c / a
Sm₃F₄S₂	405.48(2)	1936.04(9)	4.775
Eu₃F₄S₂	400.34(2)	1928.17(9)	4.816
Yb₃F₄S₂	384.61(3)	1884.2(4)	4.899

5.1.2 Oxyfluoride Sulfides of the Rare-Earth Elements

Depending on the cation radius of M^{3+} , the compounds of the sum formula $M_6O_2F_8S_3$ ($M = \text{La} - \text{Nd}, \text{Sm}$) can be obtained under the chosen reaction condition only for the rare-earth metal cations with larger radius. Compounds with the composition M_3OF_5S could be obtained and characterized by single-crystal X-ray diffraction investigations for the rare-earth elements $M = \text{Nd}, \text{Sm}$ and $\text{Gd} - \text{Ho}$, with middle radii. In addition to the two hexagonal classes of compounds, which have close mutual relations, the third structure type with the composition $M_3OF_3S_2$ ($M = \text{Y}, \text{Ho}, \text{Tm}$), preferred by the rare-earth elements with smaller ionic radius, shows a *pseudo*-tetragonal symmetry. At this point it must be mentioned, that all the three crystal structures and compound types are colorless or they are of the typical color of the related M^{3+} cations. Furthermore, because of charge neutralisation, there are "light anion" positions in all compound types, which need a mixed occupation with fluorine (as F^-) and oxygen (as O^{2-}). In contrast to the light anion positions, which are only occupied by trigonal coordinated fluoride, the positions mixed occupied by fluoride and oxide dispose of a tetragonal coordination by rare-earth(III) cations. An order of the light anions F^- and O^{2-} to the possible particle positions is shown theoretically in chapter 3.2.3.5, but it is not possible to decide which model is definitely the right one on the collected diffraction data.

$M_6O_2F_8S_3$: hexagonal, $P6_3/m$ (No. 176)			
	a / pm	c / pm	c / a
$\text{La}_6\text{O}_2\text{F}_8\text{S}_3$	1382.34(9)	397.51(2)	0.288
$\text{Ce}_6\text{O}_2\text{F}_8\text{S}_3$	1370.97(9)	392.19(2)	0.286
$\text{Pr}_6\text{O}_2\text{F}_8\text{S}_3$	1363.56(9)	389.28(2)	0.286
$\text{Nd}_6\text{O}_2\text{F}_8\text{S}_3$	1354.78(9)	386.43(2)	0.285
$\text{Sm}_6\text{O}_2\text{F}_8\text{S}_3$	1340.23(8)	381.57(2)	0.285

M₃OF₅S: hexagonal, P6₃/m (No. 176)			
	a / pm	c / pm	c / a
Nd₃OF₅S	960.71(6)	378.35(2)	0.394
Sm₃OF₅S	954.83(6)	374.62(2)	0.392
Gd₃OF₅S	948.65(5)	371.14(2)	0.391
Tb₃OF₅S	945.49(5)	369.51(2)	0.391
Dy₃OF₅S	942.37(5)	367.96(2)	0.391
Ho₃OF₅S	939.14(5)	366.53(2)	0.390

M₃OF₃S₂: tetragonal, I4/mmm (Nr. 139)			
	a / pm	c / pm	c / a-Verhältnis
Y₃OF₃S₂	384.19(3)	1898.12(17)	4.941
Ho₃OF₃S₂	383.45(3)	1894.39(17)	4.940
Tm₃OF₃S₂	380.12(3)	1889.47(17)	4.971

M₃OF₃S₂: orthorhombic, P222 (No. 16)			
	a / pm	b / pm	c / pm
Y₃OF₃S₂	542.97(5)	543.68(5)	1898.12(17)
Ho₃OF₃S₂	541.83(5)	542.74(5)	1894.39(17)
Tm₃OF₃S₂	537.28(5)	537.86(5)	1889.47(17)

5.1.3 Oxyfluorides M₅O₄F₇ (M = Gd, Yb) with *Vernier-Phase* Structure

Both compounds M₅O₄F₇ (M = Gd, Yb) have been investigated by X-ray diffraction measurements. The collected data build up a crystal structure model with the space group Abm2 (No. 39). The crystal structure is isotypical to Y₅O₄F₇ and contains three cation positions which are all differently coordinated.

M₅O₄F₇: orthorhombic, Abm2 (No. 39)			
	a / pm	b / pm	c / pm
Gd₅O₄F₇	554.16(5)	2815.7(3)	563.24(5)
Yb₅O₄F₇	532.63(5)	2736.9(3)	546.58(5)

5.1.4 Cesium Scandium Oxyfluoride CsSc₆OF₁₇

CsSc₆OF₁₇ was first obtained as a by-product during a synthesis of ScFS as a colorless, hydrolysis-insensitive crystals. The contamination of the educts with oxygen leads to the charge equation. After multiple variations of the flux, it was possible to isolate single crystals of CsSc₆OF₁₇ by washing the frozen melt. CsSc₆OF₁₇ with the hexagonal space group P6/mmm leads unconstrained to six cis edge linked [ScF₆]³⁻ octahedra. The stack of the [Sc₆F₃₀]-building blocks, built up on the fluorine anions not lying in the plane of connection forms one-dimensional hexagonal channels along [001]. Contrary to the one-dimensional elements of structure in the hexagonal rare-earth oxyfluoride sulfides and selenides, there are caesium cations in the channel structure, which are placed statistically by doubling the lattice parameters in c-direction on two crystallographically different positions.

CsSc₆OF₁₇: hexagonal, P6/mmm (No. 191)		
a / pm	c / pm	c / a
773.64(5)	802.38(5)	1.037

5.1.5 Fluoride Selenides

5.1.5.1 Tetragonal Fluoride Selenides MFSe of the A-type

This work includes the preparation and characterization of the single crystal structure of rare-earth fluoride selenides MFSe (M = La, Pr) of the A-type (matlockite structure), which are obtained by emerging an alkali chloride melt under 1000°C. In analogy to the PbFCl structure type, the M³⁺ cations are coordinated in a capped square antiprism of

four F^- and five S^{2-} anions, which are further surrounded by four and five cations. The fluoride ions themselves are tetrahedrally coordinated by four M^{3+} , whilst four edges of each tetrahedron are linked to infinite two-dimensional double layers of the composition ${}_{\infty}^2 [FM_{4/4}]^{2-}$.

MFSe: tetragonal, P4/nmm (No. 129)			
	a / pm	c / pm	c / a
LaFSe	413.79(3)	715.24(5)	1.729
PrFSe	405.31(3)	712.98(5)	1.759

5.1.5.2 Trigonal Rare-Earth(III) Fluoride Selenides M_2F_4Se

The trigonal compounds of the sum formula M_2F_4Se ($M = Ce, Pr, Nd$) were obtained as single crystals from a NaCl melt in evacuated, gas-tight, arc-welded tantalum capsules. It is to date is the fluorine richest fluoride selenide structure type of the rare-earth elements. In the Ce_2F_4Se type there are $[(F2)M_4]$ -tetrahedra, which are connected along three *cis*-standing, not coplanar M–M-edges to infinite two-dimensional double layers with the composition ${}_{\infty}^2 \{[(F1)M_{4/4}]_2^{4+}\}$. This structure element is known from the oxide selenides with the composition M_2O_2Se (trigonal, $P\bar{3}m1$) like ${}_{\infty}^2 \{[OM_{4/4}]_2^{2+}\}$ by formally substituting O^{2-} with F^- . The excess "light anions" (F^-) are placed on the one hand in the trigonal gaps and on the other hand between the edge linked $[(F1)M_4]$ -tetrahedron in the M^{3+} mono layers $(F1)^-$ (CN = 3).

M_2F_4Se: trigonal, $R\bar{3}m$ (No. 166)			
	a / pm	c / pm	c / a
Pr_2F_4Se	411.96(3)	2302.8(2)	5.590
Nd_2F_4Se	409.42(3)	2287.7(2)	5.588

5.1.6 Oxyfluoride Selenides

Two types of formula oxyfluoride selenides of the lanthanides with three different structure types were realized during this work: A-La₂OF₂Se (trigonal), M₆O₂F₈Se₃ (M = La, Nd) (hexagonal) and B-M₂OF₂Se (hexagonal). The crystal structure of the trigonal compound A-La₂OF₂Se shows not only a strong relation to the oxygen-free fluoride selenide La₂F₄Se (trigonal, R $\bar{3}$ m) but also a strong relation to the fluoride-free oxide selenide La₂O₂Se (trigonal, P $\bar{3}$ m1). The La₂OF₂Se structure of the A-type there fore can be described as an ordered intergrowth arrangement of parallelly (001) stacked, alternating La₂O₂Se and La₂F₄Se layers. On the other hand, there are the two hexagonal crystal structure types which are not constructed in the form of a stack. The compounds with the sum formula M₆O₂F₈Se₃ (M = La, Nd) crystallize isotypically to the sulfur containing rare-earth oxyfluoride sulfides M₆O₂F₈S₃. Also the structure of the compounds M₂OF₂Se of the B-type (hexagonal) with smaller cations, are closely related to this. By the loss of a fluoride-occupied "light anion" position, the coordination number of the rare-earth cations is reduced.

A-M₂OF₂Se: trigonal, R $\bar{3}$ m (No. 166)			
	a / pm	c / pm	c / a
A-La₂OF₂Se	418.13(3)	4478.2(4)	10.710

M₆O₂F₈Se₃: hexagonal, P6 ₃ /m (No. 176)			
	a / pm	c / pm	c / a
La₆O₂F₈Se₃	1394.41(9)	402.97(2)	0.289
Nd₆O₂F₈Se₃	1372.50(9)	391.36(2)	0.285

B-M₂OF₂Se: hexagonal, P6 ₃ /m (No. 176)			
	a / pm	c / pm	c / a
B-Gd₂OF₂Se	1349.24(9)	379.31(2)	0.281
B-Ho₂OF₂Se	1331.32(9)	372.13(2)	0.280

5.1.7 Fluoride Selenide Oxotantalates(V)

The compounds with the sum formula $M_2FSeTaO_4$ ($M = La$) and $M_3TaO_4F_2Se_2$ ($M = La, Nd$) are obtained by the reaction of elemental lanthanides ($M = La$ bzw. Nd) the respective trifluoride (MF_3), the sesquioxide (M_2O_3), selenium (Se) and tantalum oxide (Ta_2O_5) in the corresponding amounts with $NaCl$ as flux. In both related crystal structures of $La_2FSeTaO_4$ and $M_3F_2Se_2TaO_4$ ($M = La, Nd$) there are distorted $[TaO_5Se]$ -octahedra, which are connected over the common *trans*-oriented oxygen positions to one-dimensional chains along the b-axes. For this, all Se^{2-} ligands have an isotactic orientation. Other than the loss of a rare-earth position, of one selenide position and one fluoride position, the compounds $M_3F_2Se_2TaO_4$ ($M = La, Nd$) are more rich of one formula unit of $MFSe$ than the compounds with the sum formula $La_2FSeTaO_4$.

$M_2FSeTaO_4$: orthorhombic, Pnma (No. 62)

	a / pm	b / pm	c / pm
$La_2FSeTaO_4$	1146.51(6)	394.97(2)	1281.16(7)

$M_3F_2Se_2TaO_4$: orthorhombic, Pnma (No. 62)

	a / pm	b / pm	c / pm
$La_3F_2Se_2TaO_4$	1132.65(6)	399.84(2)	1811.66(9)
$Nd_3F_2Se_2TaO_4$	1116.53(6)	393.24(2)	1742.21(9)

5.1.8 Copper(I) Rare-Earth(II) Fluoride Chalcogenides

Both copper(I) rare-earth(II) fluoride chalcogenides CuEuFS and CuSmFSe are described as tetragonal compounds in the space group P4/nmm (Nr. 129), like CuBaFS with a filled PbFCl-type crystal structure. It is an anionic partial structure like $\infty^2 \{[\text{MF}_{4/4}\text{Ch}_{4/4}]^-\}$ with M^{2+} in square antiprismatic coordination of each four F^- and Ch^{2-} anions. For charge equilibration, Cu^+ ions are intercalated in tetrahedral holes between the Ch^{2-} double layers. CuMFCh can also be understood as a structure of layers, in which anionic layers $\infty^2 \{[\text{CuCh}_{4/4}]\}$ and analogous cationic ones $\infty^2 \{[\text{FM}_{4/4}]^+\}$ alternately stacked along (001), build up by $[\text{CuCh}_4]$ or $[\text{FM}_4]$ tetrahedra, with four connecting edges.

CuMFCh (Ch = S, Se): tetragonal, P4/nmm (Nr. 129)			
	a / pm	c / pm	c / a
CuEuFS	394.74(3)	864.25(6)	2.189
CuSmFSe	405.81(3)	881.32(7)	2.171

5.2 Prospects

The stoichiometric compounds of the rare-earth(III) fluoride sulfides (MFS) and selenides (MFSe, $\text{M}_2\text{F}_4\text{S}_2$) are structurally well characterized and partly luminescence investigations have been done on doped host lattices. More over, there are stoichiometric compositions (MOF) known as well as numerous compounds with a phase range referring the fluorine and oxygen composition ($\text{MF}_{3-x}\text{O}_{x/2}$) in the compound system of the rare-earth(III) oxide fluorides. The rare-earth(III) oxide fluoride sulfides ($\text{M}_6\text{O}_3\text{F}_8\text{S}_2$, $\text{M}_3\text{OF}_5\text{S}$ und $\text{M}_3\text{OF}_3\text{S}_2$) and selenides ($\text{M}_6\text{O}_3\text{F}_8\text{Se}_2$, A- and B- $\text{M}_3\text{OF}_5\text{Se}$) form a chain-link between both phase systems. Equally related structure elements and physical properties of both phase systems have to be investigated in the future.

6 Literatur

- [1] W. Nieuwenkamp, J. M. Bijvoet: *Z. Kristallogr.* **81** (1932) 469;
W. Nieuwenkamp: *Z. Kristallogr.* **86** (1933) 470.
- [2] F. A. Bannister, M. H. Hey: *Mineral. Mag.* **23** (1934) 587;
M. Pasero, N. Perchiazzi: *Mineral. Mag.* **60** (1996) 833.
- [3] M. Sato, M. Yamamoto, K. Imada, Y. Katsube: *J. Appl. Crystallogr.* **25** (1992) 348.
- [4] T. Jüstel, H. Nikol, C. Ronda: *Angew. Chem.* **110** (1998), 3250; *Angew. Chem. Int. Ed. Engl.* **37** (1998) 3084.
- [5] Th. Schleid: *Z. Anorg. Allg. Chem.* **626** (2000) 2429.
- [6] H. Grossholz, Th. Schleid: *Z. Kristallogr. Suppl.* **18** (2001) 109.
- [7] F. Wuttke: *Die Lichtbogen-Schweissung*, 5. Auflage, Vieweg-Verlag, Braunschweig (1968).
- [8] E. R. Wölfel: *Theorie und Praxis der Röntgenstrukturanalyse*, Vieweg-Verlag, Braunschweig (1987).
- [9] W. Massa: *Kristallstrukturbestimmung*, 2. Auflage, Teubner-Verlag, Stuttgart (1996).
- [10] Fa. STOE & Cie GmbH: *Programm WinXPOW, Version 1.04*, Darmstadt (1998).
- [11] Fa. STOE & Cie GmbH: *Programm X-SHAPE, Version 1.06*, Darmstadt (1999).
W. Herrendorf: *Programm HABITUS*, Gießen (1995).
- [12] G. M. Sheldrick: *Programm SHELXS-86*, Göttingen (1986).
- [13] G. M. Sheldrick: *Programmpaket SHELX-97*, Göttingen (1997).
- [14] G. M. Sheldrick: *Programm SHELXL-93*, Göttingen (1993).
- [15] Fa. STOE & Cie GmbH: *Programm X-RED, Version 1.19*, Darmstadt (1999).
- [16] Fa. STOE & Cie GmbH: *Programme X-STEP (Version 2.14, 1997) und X-STEP 32 (Version 1.05f, 2000)*, Darmstadt.
- [17] R. Hübenal, R. Hoppe: *Programm MAPLE 4.0*, Gießen (1995).
- [18] E. Keller: *Chem. in u. Zeit* **14** (1980) 56.

- [19] Fa. CRYSTAL IMPACT: *Programm Diamond, Version 2.1c*, Bonn (1999).
- [20] Th. Schleid: *Habilitationsschrift*, Univ. Hannover (1993).
- [21] H. Hahn, R. Schmid: *Naturwissenschaften* **52** (1965) 475;
R. Schmid, H. Hahn: *Z. Anorg. Allg. Chem.* **373** (1970) 168.
- [22] C. Dagron, F. Thévet: *C. R. Acad. Sci. Paris C* **268** (1969) 1867; *Ann. Chim. [Paris] [14]* **6** (1971) 67.
- [23] Th. Schleid: *Z. Anorg. Allg. Chem.* **625** (1999) 1700.
- [24] H. P. Beck, C. Strobel: *Z. Naturforsch.* **40 b** (1985) 1644.
- [25] F. A. Weber, Th. Schleid: *Z. Anorg. Allg. Chem.* **625** (1999) 1833.
- [26] A. F. Hollemann, E. Wiberg: *Lehrbuch der Anorganischen Chemie*, 33. Edition, Walter-de-Gruyter-Verlag, Berlin, New York (1985).
- [27] R. Hoppe: *Angew. Chem.* **78** (1966) 52; **82** (1970) 7; **92** (1980) 106; *Angew. Chem. Int. Ed. Engl.* **5** (1966) 95; **9** (1970) 25; **19** (1980) 110; *Z. Naturforsch.* **50 a** (1995) 555.
- [28] R. Hoppe: *Adv. Fluorine Chem.* **6** (1979) 387; *Izvj. Jugoslav. Centr. Krist. [Zagreb]* **8** (1973) 21; *Crystal Structure and Chemical Bonding in Inorganic Chemistry*, C. J. M. Rooymans, A. Rabenau (eds.), Amsterdam (1975); *Z. Kristallogr.* **150** (1979) 23.
- [29] H. Grossholz, Th. Schleid: *Z. Kristallogr. Suppl.* **17** (2000) 118.
- [30] H. Grossholz, Th. Schleid: *Z. Kristallogr. Suppl.* **16** (1999) 33.
H. Grossholz, Th. Schleid: *Z. Anorg. Allg. Chem.* **628** (2002) 628.
- [31] H. Grossholz, H. Müller-Bunz, Th. Schleid: *Z. Anorg. Allg. Chem.*, in Vorbereitung.
- [32] R. D. Shannon, C. T. Prewitt: *Acta Crystallogr.* **B 25** (1969) 925;
R. D. Shannon: *Acta Crystallogr.* **A 32** (1976) 751.
- [33] Th. Hahn, A. J. C. Wilson (eds.). *International Tables for Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, Boston, London (1992).
- [34] N. Rysanek, O. Loyer: *Acta Crystallogr.* **B 29** (1973) 1567.
- [35] Th. Schleid: *unveröffentlichte Ergebnisse*.
- [36] M. Folchnandt: *Dissertation*, Univ. Stuttgart (1997).
- [37] T. Petzel, O. Greis: *Z. Anorg. Allg. Chem.* **396** (1973) 95.
G. Beck, W. Nowacki: *Naturwissenschaften* **26** (1938) 495.

- [38] Th. Schleid, H. Grossholz: *Z. Anorg. Allg. Chem.* **627** (2001) 2693.
- [39] H. Lueken: *Magnetochemie*, Teubner-Verlag, Stuttgart (1999).
- [40] O. Greis, T. Petzel: *Z. Anorg. Allg. Chem.* **403** (1974) 1.
- [41] A. Zalkin, D.H. Templeton: *J. Amer. Chem. Soc.* **75** (1953) 2453.
- [42] B.V. Bukveckii, L.S. Garashina: *Koordin. Khim. [CCCP]* **3** (1977) 1024.
- [43] Th. Schleid, F. Lissner: *J. Alloys Compds.* **189** (1992) 69.
- [44] Th. Schleid, F. Lissner: *Z. Naturforsch.* **51 b** (1996) 733.
- [45] W. H. Zachariasen: *J. Chem. Phys.* **16** (1948) 254; *Acta Crystallogr.* **1** (1948) 266.
- [46] H. Gunsilius, H. Borrmann, A. Simon, W. Umland: *Z. Naturforsch.* **43 b** (1988) 1023.
- [47] M. Haase: *Z. Kristallogr.* **68** (1928) 119.
- [48] Th. Schleid, G. Meyer: *Naturwissenschaften* **76** (1989) 118.
- [49] R. Schöllhorn, W. Schramm, D. Fenske: *Angew. Chem.* **92** (1980) 477; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 492.
- [50] K. Selte, A. Kjekshus: *Acta Crystallogr.* **17** (1964) 1568;
A. F. J. Ruysink, F. Kadijk, A. J. Wagner, F. Jellinek: *Acta Crystallogr.* **B 24** (1968) 1614; J. G. Smeggil: *J. Solid State Chem.* **3** (1971) 248.
- [51] C. Sieke, I. Hartenbach, Th. Schleid: *Solid State Sci.*; in Vorbereitung.
- [52] C. Sieke, Th. Schleid: *Z. Anorg. Allg. Chem.* **627** (2001) 761.
- [53] D. Pauwels, A. Demourgues, H. Laronze, P. Gravereau, F. Guillen, O. Isnard, A. Tressaud: *Solid State Sci.* **4** (2002) 1471.
A. Demourgues, A. Tressaud, H. Laronze, P. Gravereau, P. Macaudière: *J. Fluorine Chem.* **107** (2001) 215.
- [54] W. Finkelnburg, A. Stein: *J. Chem. Phys.* **18** (1950) 1296.
W. Klemm, H. A. Klein: *Z. Anorg. Allg. Chem.* **248** (1941) 167.
- [55] J. P. Laval, A. Taoudi, A. Abaouz: *J. Solid State Chem.* **157** (2001) 134.
- [56] J. P. Laval, A. Taoudi, A. Abaouz, B. Frit: *J. Solid State Chem.* **119** (1995) 125.
- [57] B. G. Hyde, A.N. Bagshow, S. Andersson, M. O'Keeffe: *Ann. Rev. Mater. Sci.* **4** (1974) 43.
- [58] J. P. Laval, A. Taoudi, A. Abaouz, B. Frit: *J. Solid State Chem.* **119** (1995) 125.

- [59] D. J. M. Bevan, J. Mohyla, B. F. Hoskins, R. J. Steen: *Eur. J. Solid State Inorg. Chem.* **27** (1990) 451.
- [60] S. Schmid: *Acta Crystallogr.* **B 54** (1998) 391.
- [61] K. P. Reis, E. Prince, M. Stanley Whittingham: *Chem. Mater.* **4** (1992) 307; B. Gerand, G. Nowogrocki, J. Guenot, M. Figlarz: *J. Solid State Chem.* **29** (1979) 429, V. Plies: *Z. Anorg. Allg. Chem.* **521** (1985) 191.
- [62] E. Posnjak, R. W. G. Wyckoff: *J. Wash. Acad. Sci.* **12** (1922) 248; *Phys. Rev.* **21** (1923) 143.
- [63] P. P. Fedorov, V. Trncova, G. I. Kocherba, B. P. Sobolev: *Kristallografiya* **40** (1995) 716.
- [64] C. Dagrón: *Compt. Rend. Acad. Sci. Paris C* **273** (1971) 352;
Ng.-H. Dung: *Bull. Soc. Franç. Mineral. Cristallogr.* **96** (1973) 44.
- [65] Ng.-H. Dung: *Bull. Soc. Franc. Mineral. Cristallogr.* **96** (1973) 41.
- [66] Th. Schleid, M. Folchnandt: *Z. Anorg. Allg. Chem.* **622** (1996) 455.
- [67] C. Dagrón: *Compt. Rend. Acad. Sci. Paris C* **283** (1976) 743; Ng.-H. Dung:
Handbook on Physics and Chemistry of the Rare Earths, Vol. 4, North-Holland,
Amsterdam, (1979)1/88, 73/4.
- [68] Ng.-H. Dung: *Acta Crystallogr.* **B 29** (1973) 2095; Ng.-H. Dung, C. Dagrón, P. Laruelle: *Acta Crystallogr.* **B 31** (1975) 519; Ng.-H. Dung, P. Laruelle: *Acta Crystallogr.* **B 33** (1977) 3363.
- [69] Ng.-H. Dung: *Bull. Soc. Franç. Mineral. Cristallogr.* **96** (1973) 44.
- [70] M. Guittard, J. Flahaut, L. Domange: *Acta Crystallogr.* **21** (1966) 832;
F. A. Weber: *Dissertation*, Univ. Stuttgart (1999).
- [71] H. A. Eick: *Acta Crystallogr.* **13** (1960) 161.
- [72] T. D. Brennan, M. F. Mansuetto, J. A. Ibers: *J. Solid State Chem.* **107** (1993) 547.
- [73] W. J.: Zhu, Y. Z. Huang, F. Wu, C. Dong, H. Chen, Z. X. Zhao: *Mater. Res. Bull.* **29** (1994) 505.
- [74] P. Lauxmann, Th. Schleid: *Z. Anorg. Allg. Chem.* **626** (2000) 2253.
Th. Schleid, P. Lauxmann: *Z. Anorg. Allg. Chem.* **626** (2000) 2429.

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LEBENS LAUF

SENEFELDER STRASSE 96 • 70176 STUTTGART

PERSÖNLICHE INFORMATION

Familienstand:	ledig
Staatsangehörigkeit:	deutsch
Geburtsdatum:	3. Dezember 1971
Geburtsort:	Böblingen

AUSBILDUNG

1978 - 1982	Grundschule: Königsknoll, Sindelfingen
1982	Gymnasium: Stiftsgymnasium, Sindelfingen
	Abschluß: Allgemeine Hochschulreife
WS 1991/92	Beginn des Studiums der Chemie an der Universität Stuttgart
WS 1994	Abschluß der Diplomvorprüfung
WS 1997	Abschluß der Diplomprüfung
Dez. 1997 - Juni 1998	Diplomarbeit am Institut für Anorganische Chemie der Universität Stuttgart
Juli 1998	Beginn der Promotionsarbeit am Institut für Anorganische Chemie der Universität Stuttgart

TÄTIGKEITEN

Juni 1998	Wissenschaftliche Hilfskraft am Institut für Anorganische Chemie der Universität Stuttgart
Seit Juli 1998	Wissenschaftlicher Angestellter auf Zeit des Instituts für Anorganische Chemie der Universität Stuttgart

