

Suliman Nakhal* and Martin Lerch

New transition metal oxide fluorides with ReO_3 -type structure

DOI 10.1515/znb-2015-0215

Received December 18, 2015; accepted January 22, 2016

Abstract: The new niobium oxide fluorides MNbO_2F_4 [$M = (\text{Cr}, \text{Fe})$], $\text{CrNb}_2\text{O}_4\text{F}_5$, and $\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$ were prepared by treatment of chromium or iron nitrate with Nb-containing hydrofluoric acid solutions. Crystal structures were investigated by means of X-ray powder diffraction. All new compounds can be structurally refined in the cubic ReO_3 -type. The iron niobium oxide fluorides are reddish orange, and chromium containing phases exhibit a light green color. The niobium atoms are in the highest formal oxidation state.

Keywords: chromium; iron; niobium; powder diffraction; ReO_3 -type; synthesis; transition metal oxide fluorides.

Dedicated to: Professor Wolfgang Jeitschko on the occasion of his 80th birthday.

1 Introduction

Nearly all transition metal oxide fluorides are synthetic products, and many are structurally related to well-known oxide structure types such as spinel, cassiterite, ReO_3 , or garnet [1]. Some compounds are structurally derived from fluorides crystallizing in the chiolite, K_2NiF_4 , or fluorite type [1]. Transition metal oxide fluorides with rutile- or cassiterite-type structures are known for the compositions MOF ($M = \text{Ti}, \text{V}, \text{Fe}$) and $\text{M}_2\text{O}_3\text{F}$ ($M = \text{Ti}, \text{V}$). In addition, FeVO_3F , FeTiO_3F , and $\text{NbTi}_2\text{O}_5\text{F}$ have been reported [1]. Oxide fluorides based on the fluorite type are observed for lanthanide and actinide compounds [2]. Oxide fluorides of the $\text{MO}_{3-x}\text{F}_x$ type exhibiting the rhenium trioxide structure are known for $M = \text{Ti}, \text{Nb}, \text{Ta}, \text{Mo}, \text{or W}$ [3–6]. In MO_2F -type phases ($x = 1$), the M atom possesses the

highest formal oxidation state, M^{5+} . If the M cation is small (ionic radius $\sim 0.6 \text{ \AA}$) the products often crystallize in the ReO_3 -type structure or one closely related to it. In contrast, if M is larger, as in the case of the lanthanides or actinides (ionic radii $\sim 1.0 \text{ \AA}$), different structure types arise, for example the tysonite type known from LaF_3 [7]. In the case of a cubic ReO_3 -type structure the metal atoms are octahedrally coordinated by randomly distributed oxygen and fluorine atoms. The $\text{M}(\text{O},\text{F})_6$ octahedra share all six corners with adjacent octahedra. MOF_3 -type phases ($M = \text{Nb}, \text{Ta}$) have also been described, crystallizing in structures related to the SnF_4 type [8].

It should be mentioned that transition metal oxide fluorides are of interest as cathode materials for lithium ion batteries (e.g. [9]). The voltage of batteries using transition metal oxide fluoride- or transition metal fluoride-based cathode masses is expected to be higher compared to that of the corresponding oxides for the same redox pair [10]. In addition, oxide fluorides have also been found to be promising laser hosts and fluorescent materials for optical applications [11].

Recently a series of new mixed metal oxide fluorides $\text{MNb}_2\text{O}_3\text{F}_6$ ($M = \text{Mg}, \text{Zn}$), MgM_2OF_8 ($M = \text{Ti}, \text{Zr}$), $\text{Fe}_2\text{TiO}_8\text{F}$, and $\text{TiNb}_2\text{O}_5\text{F}_4$ has been reported [12]. These compounds crystallize in the ReO_3 -type ($\text{MNb}_2\text{O}_3\text{F}_6$, $M = \text{Mg}, \text{Zn}$) and related structures, for example the NaSbF_6 type (MgTi_2OF_8 and MgZr_2OF_8) or the VF_3 type (Fe_2TiOF_8). In the present contribution we report on the syntheses and crystal structures of previously unknown mixed metal oxide fluorides MNbO_2F_4 ($M = \text{Cr}, \text{Fe}$), $\text{CrNb}_2\text{O}_4\text{F}_5$, and $\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$.

2 Results and discussion

All oxide fluorides presented here were prepared by the method reported by Permer and Lundberg [13], originally used for the synthesis of TiOF_2 and NbO_2F . In a first step, 0.5 g niobium oxide Nb_2O_5 (Fluka 99%) was added to 3 mL HF (aq.) (Merck, 48%). In a second step, a stoichiometric amount of chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich 99%) or iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich 99.99%) was added to the niobium fluoride suspension and the mixture stirred for 15 h in a Teflon beaker. Slow evaporation (80°C ,

*Corresponding author: Suliman Nakhal, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany, Fax: +49 30 314 79656, E-mail: s.nakhal@chem.tu-berlin.de
Martin Lerch: Institut für Chemie, Technische Universität Berlin, D-10623 Berlin, Germany

2 days) of the resulting mixture to dryness using a hot plate yielded the respective crystalline oxide fluorides. The remaining powders were washed several times with ethanol and afterwards dried at temperatures between 150 and 200°C in an inert atmosphere. Phase-pure MNbO_2F_4 ($M = \text{Fe}, \text{Cr}$), $\text{CrNb}_2\text{O}_4\text{F}_5$, and $\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$ were synthesized. The CrNbO_2F_4 powder still contains ~ 3 wt% CrNbO_4 as a second phase. For all prepared samples the analytically determined compositions (see Experimental section) fit well with the given formulas. No indication for significant amounts of hydrogen was found for any sample.

The crystal structures of the new phases were refined using conventional X-ray powder techniques (for details see Experimental part). In general, due to their positions in the periodic table, the elements oxygen and fluorine cannot be distinguished using X-ray methods. Unfortunately, also for neutron diffraction the coherent scattering lengths are very similar: $b_{\text{O}} = 5.803$ fm, $b_{\text{F}} = 5.654$ fm. Consequently, we will not give experimental results concerning O/F order and treat oxygen and fluorine as statistically distributed. It is evident that the real crystal structures may be of lower symmetry (non-cubic) than that presented. However, it should be mentioned that no indications for symmetry reduction could be derived from the observed metrics. The X-ray powder diffraction patterns of the finally obtained oxide fluorides are presented in Figs. 1–4. All crystal structures could easily be refined in the cubic ReO_3 -type (space group $Pm\bar{3}m$, cations on $1a$ (0, 0, 0), anions on $3d$ ($1/2$, 0, 0) positions) also known from TiOF_2 , MO_2F ($M = \text{Nb}, \text{Ta}$) [4, 5], ($\text{MNb}_2\text{O}_3\text{F}_6$ ($M = \text{Mg}, \text{Zn}$)), MgTiOF_8 , and $\text{TiNb}_2\text{O}_5\text{F}_4$ [12]. As commonly known, the ReO_3 -type structure can be described as a continuous 3D array of vertex-sharing octahedra (Fig. 5). As explained

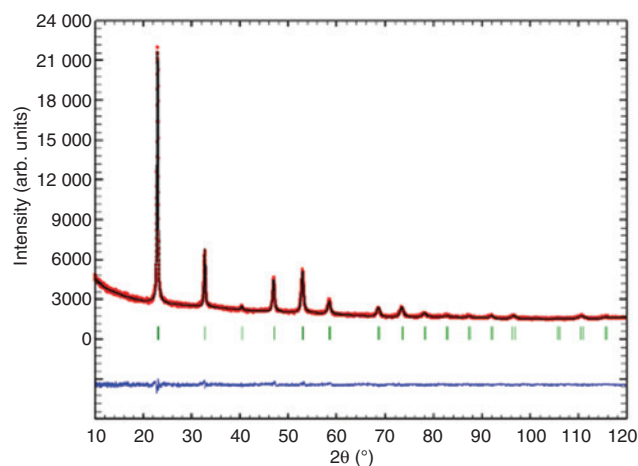


Fig. 2: Powder X-ray diffraction diagram of $\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$ with the results of the Rietveld refinement.

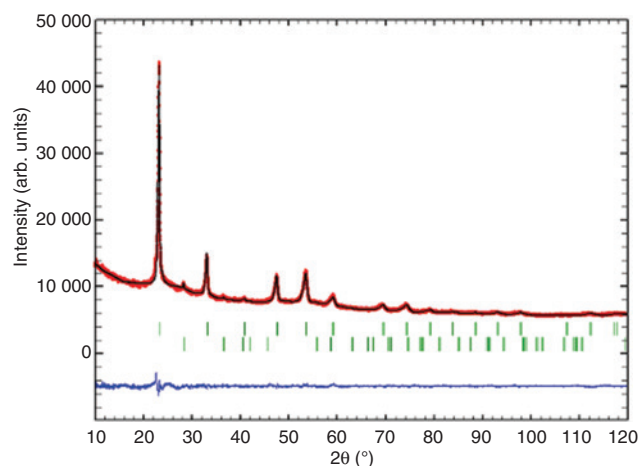


Fig. 3: Powder X-ray diffraction diagram of CrNbO_2F_4 with the results of the Rietveld refinement (markers: CrNbO_2F_4 , top; ~ 3 wt% CrNbO_4 , bottom).

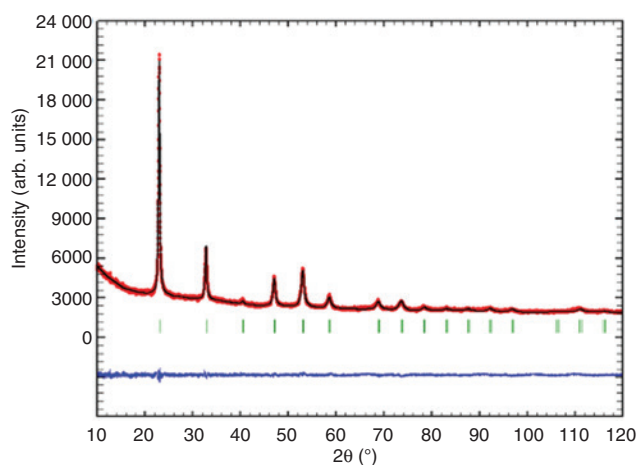


Fig. 1: Powder X-ray diffraction diagram of FeNbO_2F_4 with the results of the Rietveld refinement.

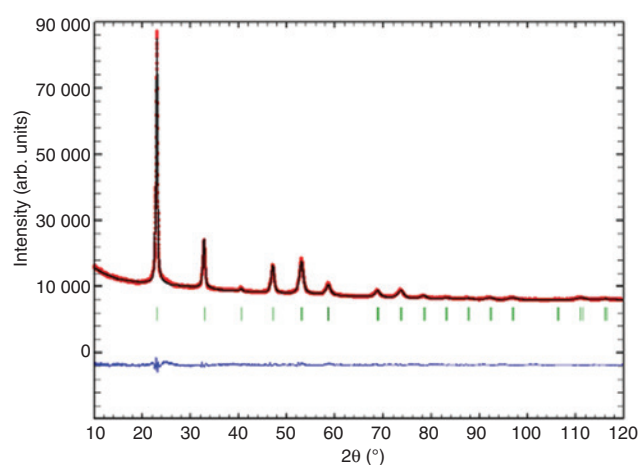


Fig. 4: Powder X-ray diffraction diagram of $\text{CrNb}_2\text{O}_4\text{F}_5$ with the results of the Rietveld refinement.

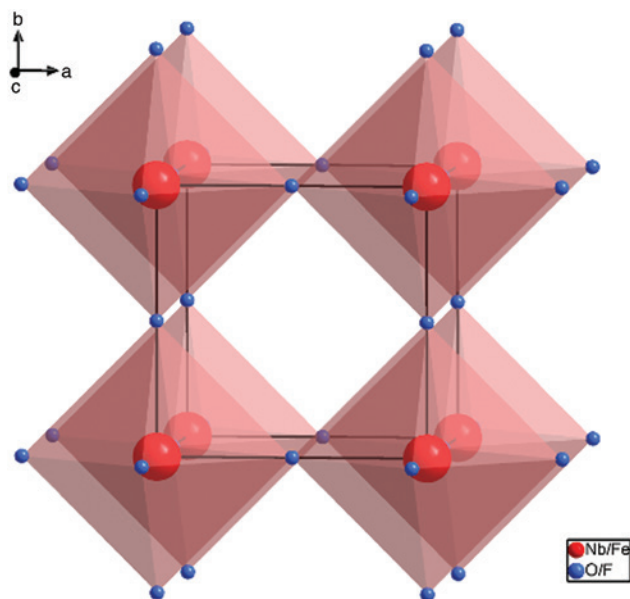


Fig. 5: Unit cell of the cubic ReO_3 -type (e.g. FeNbO_2F_4), outlined by black lines, showing the $(\text{Nb/Fe})(\text{O/F})_6$ polyhedra.

above, all oxide fluorides with this structure were refined assuming a random distribution of fluorine and oxygen on the anion sites. The final structural parameters are presented in Tables 1–3, the average bond lengths between metal cations and the surrounding anions in Table 4. In order to give an integer value for Z (number of formula units in the unit cell), the chemical compositions presented in Tables 1 and 2 are normalized to one cation and three anions (ReO_3 -type).

The refined site occupation factors are in good agreement with the chemical formulas (Table 3). In addition,

Table 1: Crystal structure data of crystalline FeNbO_2F_4 and $\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$ powders (ReO_3 -type, space group $Pm\bar{3}m$).

	1	2
Formula	FeNbO_2F_4 ($\text{Fe}_{0.5}\text{Nb}_{0.5}\text{OF}_2$)	$\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$ ($\text{Fe}_{0.4}\text{Nb}_{0.6}\text{O}_{1.2}\text{F}_{1.8}$)
M_r	128.36	131.47
a , pm	385.58(2)	386.534(14)
V , pm^3	$57.324(4) \times 10^6$	$57.751(4) \times 10^6$
Z	1	1
$D_{\text{calcd.}}$, g cm^{-3}	3.72	3.78
2θ range, deg	10–120	10–120
R_{wp}	0.020	0.024
R_{exp}	0.019	0.021
R_{Bragg}	0.027	0.035
R_p	0.016	0.018
R_F	0.027	0.034
S	1.05	1.14

Table 2: Crystal structure data of crystalline CrNbO_2F_4 and $\text{CrNb}_2\text{O}_4\text{F}_5$ powders (ReO_3 -type, space group $Pm\bar{3}m$).

	1	2
Formula	CrNbO_2F_4 ($\text{Cr}_{0.5}\text{Nb}_{0.5}\text{OF}_2$)	$\text{CrNb}_2\text{O}_4\text{F}_5$ ($\text{Cr}_{0.33}\text{Nb}_{0.67}\text{O}_{1.33}\text{F}_{1.67}$)
M_r	126.43	132.26
a , pm	383.12(2)	385.46(4)
V , pm^3	$56.235(6) \times 10^6$	$57.269(10) \times 10^6$
Z	1	1
$D_{\text{calcd.}}$, g cm^{-3}	3.73	3.83
2θ range, deg	10–120	10–120
R_{wp}	0.017	0.019
R_{exp}	0.011	0.011
R_{Bragg}	0.028	0.036
R_p	0.013	0.014
R_F	0.017	0.021
S	1.55	1.73

Table 3: Refined atomic coordinates, isotropic Debye–Waller factors and site occupations for all oxide fluorides.

Compound	Wyckoff site	B_{iso} (\AA^2)	s.o.f
$\text{Cr}_{0.5}\text{Nb}_{0.5}\text{OF}_2$ (CrNbO_2F_4)	Cr/Nb: 1a	0.38(2)	Cr: 0.489(9) Nb: 0.510(9)
	O/F: 3d	1.80(9)	0.333/0.667 ^a
$\text{Cr}_{0.33}\text{Nb}_{0.67}\text{O}_{1.33}\text{F}_{1.67}$ ($\text{CrNb}_2\text{O}_4\text{F}_5$)	Cr/Nb: 1a	0.30(2)	Cr: 0.33(3) Nb: 0.67(3)
	O/F: 3d	2.06(16)	0.444/0.556 ^a
$\text{Fe}_{0.5}\text{Nb}_{0.5}\text{OF}_2$ (FeNbO_2F_4)	Fe/Nb: 1a	0.12(2)	Fe: 0.501(12) Nb: 0.498(12)
	O/F: 3d	2.19(10)	0.333/0.667 ^a
$\text{Fe}_{0.4}\text{Nb}_{0.6}\text{O}_{1.2}\text{F}_{1.8}$ ($\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$)	Fe/Nb: 1a	0.40(6)	Fe: 0.396(9) Nb: 0.603(9)
	O/F: 3d	1.22(9)	0.4/0.6 ^a

^aNot refined, values taken from chemical composition.

comparing the determined bond lengths with reported values from the literature for pure oxides and fluorides it can be stated that the results for the oxide fluorides are in good agreement with the average values for the oxides/fluorides in the respective compositions (Table 4). As an example, for FeNbO_2F_4 the refined bond length of 192.8 pm fits well to the average value calculated from NbF_5 , FeF_3 , and FeNbO_4 : 193.8 pm. $\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$ exhibits a refined bond length of 193.3 pm. The value calculated from the fluorides and the oxide is 194.1 pm. Also for chromium niobium oxide fluorides the refined bond lengths fit well to the average values calculated from NbF_5 , CrF_3 , and CrNbO_4 . A bond length of 191.4 pm has experimentally been determined for CrNbO_2F_4 , 191.6 pm has been calculated. Finally, $\text{CrNb}_2\text{O}_4\text{F}_5$ shows 192.7 pm (refined) as

Table 4: Experimentally determined average bond lengths between cations and surrounding anions and values reported for oxides and fluorides for comparison.^a

Compound	Determined				Found ^a
	$d_{(\text{Cr/Nb})-(\text{O/F})}$	$d_{(\text{Cr/Nb})-(\text{O})}$	$d_{(\text{Nb/F})}$	$d_{(\text{Cr-F})}$	
CrNbO_2F_4	191.56(2)	198.6 (CrNbO_4)	187.3 (NbF_5)	189.9 (CrF_3)	
$\text{CrNb}_2\text{O}_4\text{F}_5$	192.73(2)	198.6 (CrNbO_4)	187.3 (NbF_5)	189.9 (CrF_3)	
	$d_{(\text{Fe/Nb})-(\text{O/F})}$	$d_{(\text{Fe/Nb})-(\text{O})}$	$d_{(\text{Nb/F})}$	$d_{(\text{Fe-F})}$	
FeNbO_2F_4	192.79(2)	198.9 (FeNbO_4)	187.3 (NbF_5)	192.3 (FeF_3)	
$\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$	193.27(2)	198.9 (FeNbO_4)	187.3 (NbF_5)	192.3 (FeF_3)	

^aReported values taken from CrNbO_4 [14], NbF_5 [15], CrF_3 [16], FeNbO_4 [17], FeF_3 [18].

compared to 193.5 pm (calculated). As already mentioned in the Introduction, small M cations (ionic radii $\sim 0.6 \text{ \AA}$) lead to products crystallizing in the ReO_3 structure or one closely related to it. As described, all metal oxide fluorides presented in this contribution crystallize in the ReO_3 -type structure. This is no surprise because the effective ionic radii for Nb^{5+} , Cr^{3+} , and Fe^{3+} (coordination number 6) are 64, 61.5, and 64.5 pm, respectively [19].

3 Experimental section

3.1 Chemical characterization and crystal structure refinement

The powders were chemically characterized by combustion analysis (Thermo Finnigan FlashEA 1112 NC analyzer for hydrogen content). The amount of oxygen was determined using a LECO EF-TC 300 N_2/O_2 analyzer, hot gas extraction method). In addition, X-ray fluorescence analysis (PANalytical Axios PW4400/24 X-ray fluorescence spectrometer with an Rh tube and wavelength-dispersive detection) was used to check the metal contents.

Anal. found: $\text{Cr:Nb} = 19.7:36.2$, and $12.8 \pm 0.3 \text{ wt\%}$ for oxygen in CrNbO_2F_4 , calcd. $\text{Cr:Nb} = 20.6:36.7$, and 12.7 wt\% for oxygen. For $\text{CrNb}_2\text{O}_4\text{F}_5$ we found $\text{Cr:Nb} = 12.8:46.4$, and $16.4 \pm 0.3 \text{ wt\%}$ oxygen, calcd. $\text{Cr:Nb} = 13.1:46.8$, and 16.1 wt\% for oxygen. For FeNbO_2F_4 the analysis results are $\text{Fe:Nb} = 21.5:35.9$, and $12.4 \pm 0.3 \text{ wt\%}$ for oxygen, calcd. $\text{Fe:Nb} = 21.8:36.2$, and 12.5 wt\% for oxygen. For $\text{Fe}_2\text{Nb}_3\text{O}_6\text{F}_9$ we found $\text{Fe:Nb} = 17.2:40.9$, and $14.4 \pm 0.3 \text{ wt\%}$ oxygen, calcd. $\text{Fe:Nb} = 17.0:42.4$, and 14.6 wt\% for oxygen. Thus, the analytical results are in good agreement with the expected compositions for the prepared oxide fluorides.

A PANalytical X'Pert PRO MPD diffractometer (CuK_α radiation, Bragg–Brentano (θ - θ) geometry) with a PIXcel detector was used for the powder XRD measurements

at ambient temperature. For Rietveld refinements, the program package FULLPROF [20] was used. The background was manually defined. Reflection profiles were fitted with a pseudo-Voigt function (Gaussian parameters U , V , and W ; Lorentzian parameter X ; mixing parameter η). Asymmetry was corrected for using the Bérar–Baldinozzi method with two parameters [21].

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html), on quoting the deposition numbers CSD-430926 ($\text{Fe}_{0.5}\text{Nb}_{0.5}\text{OF}_2$), CSD-430927 ($\text{Fe}_{0.4}\text{Nb}_{0.6}\text{O}_{1.2}\text{F}_{1.8}$), CSD-430928 ($\text{Cr}_{0.5}\text{Nb}_{0.5}\text{OF}_2$), and CSD-430929 ($\text{Cr}_{0.33}\text{Nb}_{0.67}\text{O}_{1.33}\text{F}_{1.67}$).

4 Conclusion

The simple synthesis route described in our contribution allows the preparation of various mixed metal oxide fluorides and appears to be a promising pathway to yet unknown compounds. This may also be of interest for the preparation of new cathode materials for lithium ion batteries with improved electrochemical properties (higher voltage of the battery etc.). All transition metal oxide fluorides presented in this work crystallize in the ReO_3 -type. In the near future we will report on oxide fluorides exhibiting the rutile- or fluorite-type structure.

Acknowledgments: Financial support of the German Ministry of Education and Research (BMBF) within the LIB 2015 initiative (HE-Lion) and the Deutsche Forschungsgemeinschaft (DFG, SPP 1415) is gratefully acknowledged. We also thank Dipl.-Chem. Steven Orthmann and Dr. Rafael Zubrzycki (TU Berlin) for performing oxygen analyses (S. O.) and X-ray fluorescence analyses (R. Z.).

References

- [1] P. Hagemuller, *Inorganic Solid Fluorides*, Academic Press, Inc., Orlando, **1985**.
- [2] M. Takashima, in *Advanced Inorganic Fluorides*, Vol. 7 (Eds.: T. Nakajima, B. Zemva, A. Tressaud), Elsevier Science S. A., Lausanne, **2000**, chapter 16, p. 175.
- [3] D. Bable, in *Structure and Bonding*, Vol. 111, (Ed.: C. K. Jorgensen), Springer-Verlag, New York, NY, **1967**, p. 37.
- [4] K. Vorres, J. Donohue, *Acta Crystallogr.* **1955**, 8, 25.
- [5] H. Schäfer, H. G. Schnering, K. J. Niehues, H. G. Nieder-Vaharenholz, *J. Less-Common Met.* **1965**, 9, 95.
- [6] D. E. LaValle, R. M. Steele, M. K. Wilkinson, H. L. Yakel, *J. Am. Chem. Soc.* **1960**, 82, 2433.
- [7] T. I. Dyuzheva, L. M. Lityagina, G. B. Demishev, N. A. Bendeliani, *J. Alloys Compd.* **2002**, 335, 59.
- [8] J. Köhler, A. Simon, L. van Wüllen, S. Cordier, T. Roisnel, M. Poulain, M. Somer, *Z. Anorg. Allg. Chem.* **2002**, 628, 2683.
- [9] E. Gonzalo, A. Kuhn, F. Garcia-Avarado, *J. Power Sources* **2010**, 195, 4990.
- [10] Y. Koyama, I. Tanaka, H. Adachi, *J. Electrochem. Soc.* **2000**, 147, 3633.
- [11] H. Yu, H. Guo, M. Zhang, Y. Liu, M. Liu, L.-J. Zhao, *Nanoscale Res. Lett.* **2012**, 7, 275.
- [12] S. Nakhal, T. Bredow, M. Lerch, *Z. Anorg. Allg. Chem.* **2015**, 641, 1036.
- [13] L. Permer, M. Lundberg, *J. Solid State Chem.* **1989**, 81, 21.
- [14] A. Petersen, H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **1992**, 609, 51.
- [15] A. J. Edwards, *J. Chem. Soc.* **1964**, 3714. DOI: 10.1039/JR9640003714.
- [16] K. Knox, *Acta Crystallogr.* **1960**, 13, 507.
- [17] M. Harder, H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **1979**, 456, 99.
- [18] M. Leblanc, J. Pannetier, G. Ferey, R. de Pape, *Phase Trans.* **1992**, 38, 127.
- [19] R. D. Shannon, *Acta Crystallogr.* **1976**, A32, 751.
- [20] J. Rodríguez-Carvajal, *Physica B: Condens. Matter* **1993**, 192, 55.
- [21] J.-F. Béar, G. Baldinozzi, *J. Appl. Crystallogr.* **1993**, 26, 128.