Preparation and Crystal Structure of a New Lithium Vanadium Fluoride Li_2VF_6 with Trirutile-type Structure

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A new lithium vanadium fluoride Li_2VF_6 was prepared by reacting lithium fluoride LiF with vanadium tetrafluoride VF_4 in a monel capsule at 500 °C. The crystal structure has been determined by means of powder X-ray diffraction. Trirutile-type dilithium hexafluorovanadate(IV) crystallizes in the tetragonal space group $P4_2/mnm$ with lattice parameters $a = 459.99(1)$, $b = 459.99(1)$, $c = 896.64(2)$ pm. The presence of a Jahn-Teller effect is discussed.

Key words: Lithium Metal Fluoride, Synthesis, Crystal Structure

Introduction

Numerous ternary fluorides of the formula type A_2MF_6 (A = alkali metal, M = main group element or transition metal) with larger alkali ions are known. The crystal chemistry of these compounds, often crystallizing in several modifications, has been discussed for more than 60 years [1 – 3]. There were only few reports on compounds containing the small alkali ion lithium. For most of the oxidation states of d-transition metal ions the ratio of the ionic radii r_M/r_F is within the range 0.41 – 0.73 [4]. Most of the reported compounds with A_2MF_6 composition crystallize in the following structure types or are closely related to them: Li_2ZrF_6, Na_2SiF_6, trirutile. Differences arise from the type of atom sharing between the coordination octahedra: a) Li_2ZrF_6 type (trigonal, space group $P\bar{3}1m$): solely corner-sharing between $A^{I}F_6$ and $M^{IV}F_6$ octahedra. b) Na_2SiF_6 type (trigonal, space group $P321$): SiF_6 units share three edges with NaF_6 octahedra. c) trirutile type (tetragonal, $P4_2/mnm$) and related structures (*e. g.* $CuSb_2O_6$ type, monoclinic, spacegroup $P2_1/n$) [5]: only two common edges.

It should be mentioned that ternary lithium metal fluorides are of interest as cathodes for lithium ion batteries. The voltage of batteries using transition metal fluoride-based cathode masses is expected to be higher as compared to the corresponding oxides for the same redox pair [6].

For lithium vanadium fluorides the following phases have been reported in literature: cryolite type-related orthorhombic α- and monoclinic β-$Li_3V^{(III)}F_6$ [7], $LiV_2^{(II/III)}F_6$ (tetragonal, a mixed-valence trirutile structure) [8], and $LiV^{(V)}F_6$ (rhombohedral, $LiSbF_6$ type) [9]. In this contribution we report on the synthesis and the crystal structure of the new lithium vanadium fluoride $Li_2V^{(IV)}F_6$.

Experimental Section

For the synthesis of Li_2VF_6 710 mg vanadium tetrafluoride powder (ABCR, 95 %) and 290 mg lithium fluoride (Alfa Aesar, 99.9 %), which were used as starting materials, were dried under vacuum at 250 °C for 24 h. The mixture of LiF and VF_4 (2:1 molar ratio) was heated at 500 °C for 12 h in a monel capsule and then slowly cooled to ambient temperature. The powder was chemically characterized using a Leco EF-TC 300 N_2/O_2 analyzer (hot gas extraction) for oxygen content determination. Detection of remaining capsule material was carried out by X-ray fluorescence analysis (PANalytical Axios PW4400/24 X-ray fluorescence spectrometer with an Rh tube and a wavelength dispersive detector). 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 measure-

ments at ambient temperature, the program package FULLPROF 2006 [10, 11] for Rietveld refinements. Peak profiles were fitted with a pseudo-Voigt function.

Results and Discussion

Following the instructions described in the experimental section, a greenish-yellow powder can be prepared. X-Ray fluorescence measurements give no indication for Cu or Ni (capsule materials) to be present in the obtained product. In addition, no significant amount of oxygen was detected. Analyzing the powder X-ray patterns depicted in Fig. 1, a yet unknown phase together with β-Li_3VF_6 is observed. The crystal structure of the new phase was determined using conventional powder X-ray techniques and found to be isotypic to Li_2CrF_6. This hexafluorochromate(IV) was structurally described for the first time by Siebert and Hoppe [12] and reported to be of the Na_2SnF_6 type, a monoclinically distorted trirutile derivative. Later on the crystal structure of Na_2SnF_6 was in the focus of discussion. Bournonville *et al.* pointed out the relationships between the monoclinic Na_2SnF_6 and the tetragonal trirutile type [13], showing that they are identical within the limits of a probable error. Some years later Benner and Hoppe [14] presented a structure redetermination of Na_2SnF_6 preferring the tetragonal trirutile type. Recently also Li_2CrF_6 was reported to be tetragonal [15]. A more detailed discussion of these problems together with a deep insight into the crystal chemistry of the rutile type and its derivatives, including the trirutile type, was presented by Baur [16]. Re-

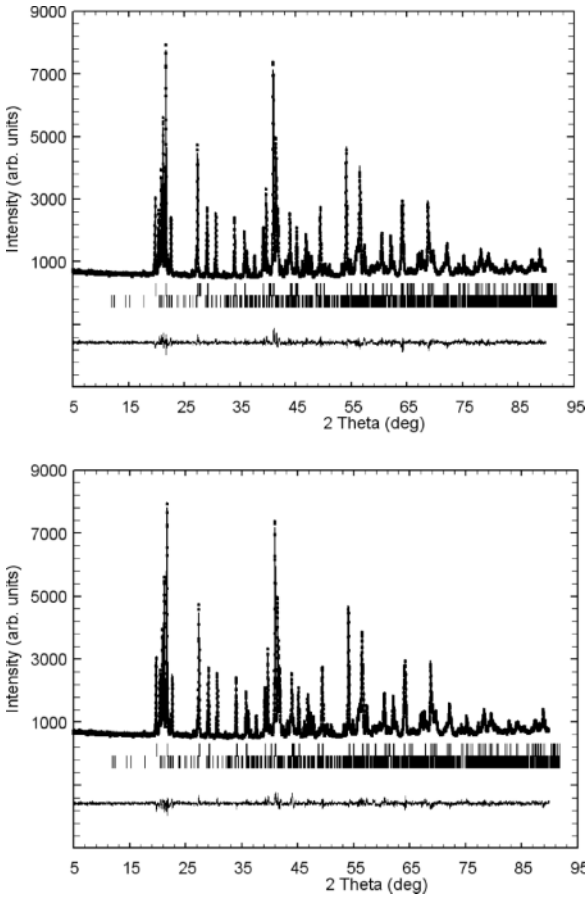

Fig. 1. Powder X-ray diagram of Li_2VF_6 with the results of the Rietveld refinements (markers: Li_2VF_6, top; β-Li_3VF_6, bottom). Upper image: monoclinic model, below: tetragonal trirutile model.

Table 1. Refined parameters for Li_2VF_6 at ambient temperature (comparison between the monoclinic 'Na_2SnF_6' and the tetragonal trirutile model).

Structure type	'Na_2SnF_6'	Trirutile
Space group	$P2_1/c$ (no. 14)	$P4_2/mnm$ (no. 136)
Crystal system	monoclinic	tetragonal
M_r	389.94	
a, pm	459.91(2)	459.99(1)
b, pm	459.76(3)	459.99(1)
c, pm	1007.43(4)	896.64(2)
β, deg	117.16(4)	90
V, pm^3	$189.54(2) \times 10^6$	$189.72(1) \times 10^6$
Refined parameters	32	23
Z	2	2
2θ range, deg	5 – 90	5 – 90
R_{wp}	0.0453	0.0473
R_{Bragg}	0.0481	0.0501
R_{exp}	0.0340	0.0340
S	1.33	1.39

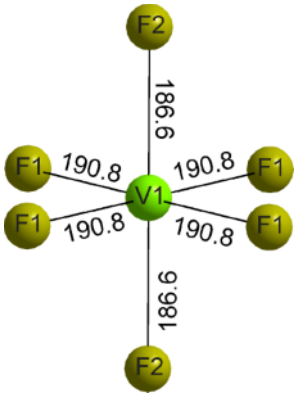

Fig. 2 (color online). VF_6 polyhedron with the determined bond lengths (pm).

Table 2. Refined structural parameters for Li_2VF_6 at ambient temperature (comparison between the monoclinic 'Na_2SnF_6' (top) and the tetragonal trirutile (bottom) model).

Atom	Wyckoff site	x	y	z	B_{iso} (Å^2)
V	2*a*	0	0	0	0.66(9)
Li	4*e*	0.340[a]	−0.028[a]	0.336[a]	0.85
F1	4*e*	0.2878(5)	0.2787(4)	−0.0011(2)	0.8(2)
F2	4*e*	−0.0153(6)	0.1998(2)	0.0011(2)	1.3(2)
F3	4*e*	0.3304(3)	0.765(6)	0.1521(4)	1.9(2)

[a] Not refined, data taken from Li_2CrF_6 [12].

Atom	Wyckoff site	x	y	z	B_{iso} (Å^2)
V	2*b*	0	0	0.5	0.42(5)
Li	4*e*	0	0	0.1646[a]	0.7
F1	8*j*	0.1979(3)	0.1979(3)	0.3429(2)	0.41(7)
F2	4*f*	−0.2868(4)	0.2868(4)	0.5	0.72(9)

[a] Not refined, data taken from Li_2CrF_6 [15].

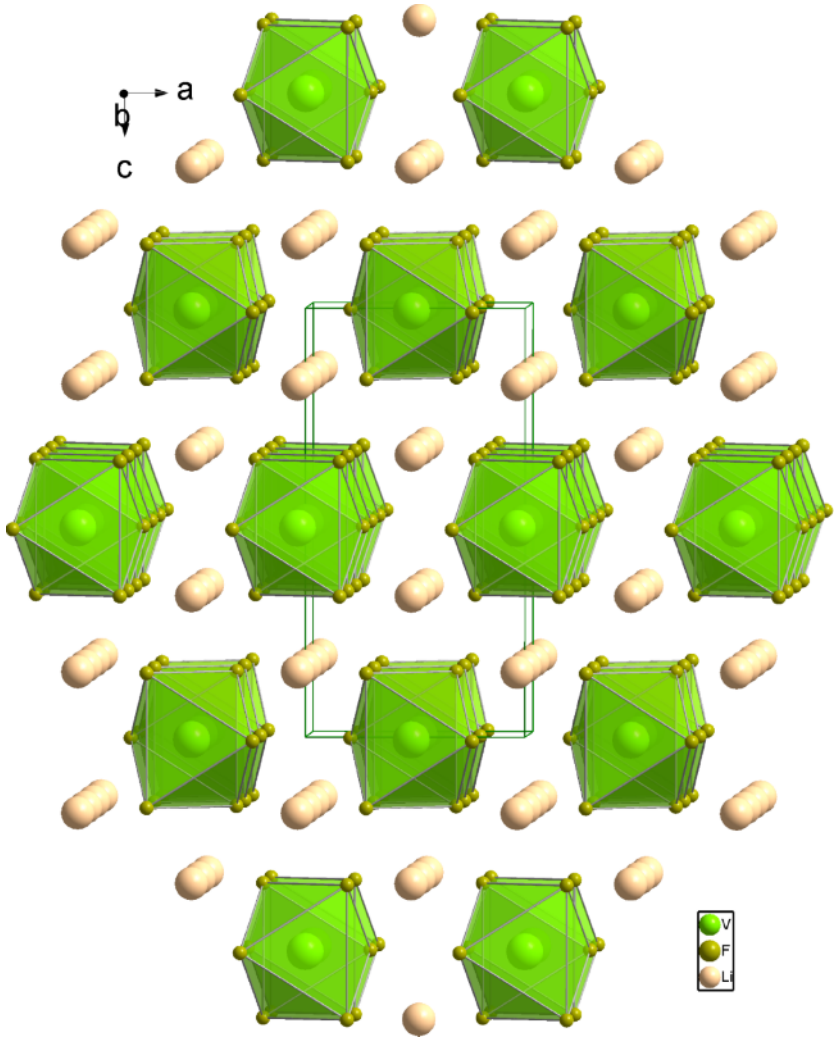

Fig. 3 (color online). Unit cell of trirutile-type Li_2VF_6, outlined by green lines, together with the VF_6 polyhedra.

specting these contributions, Rietveld refinements of the structural parameters of the new dilithium hexafluorovanadate(IV) were performed using the tetragonal trirutile as well as the monoclinic 'Na_2SnF_6' model. The results of the Rietveld refinements are presented in Fig. 1 as well as in Tables 1 and 2. An amount of $\approx$ 41 wt-% β-Li_3VF_6 as a second phase is observed. This may be explained by partial decomposition of VF_4 and significant amounts of VF_3 in the starting material. In our refinement procedure the atomic positions of lithium were not refined but taken from Li_2CrF_6 [12, 15]. Comparing the results of both models it is evident that the monoclinic description leads to slightly better R values. Nevertheless, respecting the limitations of powder methods and the presence of such large amounts of a second phase with low symmetry (monoclinic) the use of the tetragonal trirutile model seemed to be more reasonable. In the following we discuss the crystal structure of Li_2VF_6 in the light of the structure type with higher symmetry.

In respect to the well-known trirutile type, which can be understood as superstructure of the rutile type with a tripled c cell parameter and an ordered arrangement of the cations (same space group type), the crystal structure of dilithium hexafluorovanadate(IV) can be described in the following way: vanadium occupies the 2b position, lithium the 4e, and fluorine the positions 4f and 8j (see Table 2). The crystal structure is built up from isolated slightly compressed VF_6 octahedra (V–F: $2 \times 186.6(2)$ pm, $4 \times 190.8(2)$ pm, Fig. 2) connected by lithium atoms also coordinated by six fluorine atoms (see Figs. 3, 4). The polyhedra share two opposing edges leading to straight chains along the tetragonal c axis, each of them surrounded by four other chains sharing common vertices. The average bond length between vanadium and the surrounding anions, d_{V-F}, is 189 pm, which is slightly longer compared to the reported V–F bond length in VF_4 ($d_{V-F} = 185$ pm) [17]. To answer the question whether the compression of the VF_6 octahedra is mainly caused by next nearest neighbors connecting the polyhedra to the above-described framework or by a relatively weak Jahn-Teller effect (keep in mind that V^{4+} has a d^1 configuration), a short look at the crystal struc-

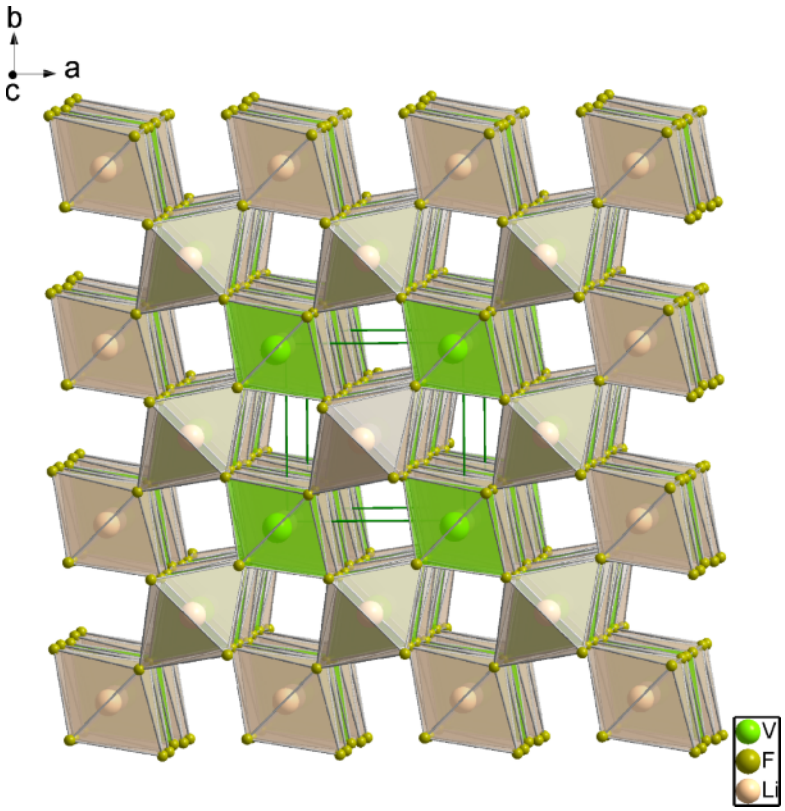

Fig. 4 (color online). Connectivity between VF_6 and LiF_6 polyhedra. The tetragonal unit cell is outlined by green lines.

tures of $Li_2Ti^{(IV)}F_6$ (trirutile type, d^0 configuration) and the halides of titanium in lower oxidation states (in particular Ti^{3+}, d^1 configuration) may be helpful. A general overview of the latter is given by Meyer *et al.* [18] and, from a more physical point of view, by Khomskii and Mostovoy [19]. Trilithium hexafluorotitanate(III) is known to exist in two polymorphs [20], an orthorhombic α-form and a monoclinic β-form. The latter was structurally investigated by Tyagi *et al.* [21], also discussing the presence of a Jahn-Teller distortion of the TiF_6 octahedra. From a comparison with β-Li_3AlF_6 they concluded that the distortions within the TiF_6 octahedra are mainly caused by the surrounding Li polyhedra, and a static Jahn-Teller effect plays only a negligible role [22]. For α-Li_3TiF_6, crystallizing closely related to the cryolite-type structure, only one kind of TiF_6 octahedra exists, showing interatomic distances in the range of 193 – 227 pm but no clear compression or elongation of the octahedra [23]. For the corresponding aluminum compound α-Li_3AlF_6 (d^0 configuration) only a slight distortion of the AlF_6 octahedra is reported (Al–F bond lengths between 179 and 183 pm) [24]. However, a comparison between the crystal structures of $Li_2V^{(IV)}F_6$ (d^1) and $Li_2Ti^{(IV)}F_6$ (d^0) is most helpful for understanding the effect of polyhedra connection, because both compounds crystallize in the tetragonal trirutile type. As described above, the V–F bond lengths in Li_2VF_6 are $2 \times 186.6(2)$ pm and $4 \times 190.8(2)$ pm. The corresponding Ti–F values in Li_2TiF_6 are $2 \times 189.2(9)$ pm and $4 \times 194.7(6)$ pm [25]. These findings strongly indicate that the observed compression of the VF_6 octahedra is mainly caused by next-nearest neighbor connections and not by a Jahn-Teller effect.

In the Li_2MF_6 series the stability range of the different phases at ambient and high pressure has been correlated with the ionic radii of the involved tetravalent cations [26]: Na_2SiF_6 type: $r_M^{4+} \leq 0.54$ Å; trirutile type: $r_M^{4+}/54 < r < 71$ pm, Li_2ZrF_6 type: $r_M^{4+} \geq 71$ pm. As expected, the number of common edges connecting polyhedra decreases with increasing size of the M cation. Respecting these findings, the observed trirutile type for Li_2VF_6 ($r_V^{4+} = 58$ pm [27]) is not surprising.

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