# Redetermination of the crystal structure of heptalithium tetranitridovanadate(V), $Li_7[VN_4]$

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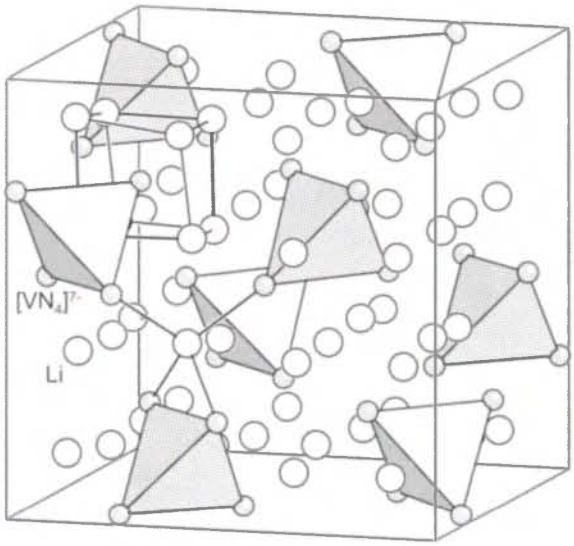


## Abstract

$Li_7N_4V$, cubic, $Pa\bar{3}$ (No. 205), $a = 9.599(2)$ Å, $V = 884.5$ Å$^3$, $Z = 8$, $R_{gt}(F) = 0.054$, $wR_{ref}(F^2) = 0.104$, $T = 293$ K.

## Source of material

$Li_7[VN_4]$ was prepared from stoichiometric amounts of $Li_3N$ and V under nitrogen of ambient pressure at 1173 K. Crystals were grown from the melt (excess Li) under Ar by cooling from 1373 K.

## Discussion

$Li_7[VN_4]$ was first reported to crystallize with a $CaF_2$-type superstructure in the space group $P\bar{4}3n$ [1,2]. The same space group was found for $Li_7[MnN_4]$ [2]. $Li_7[NbN_4]$ [3] and $Li_7[TaN_4]$ [4] also crystallize with a $CaF_2$- type superstructure, but in the space group $Pa\bar{3}$.

The X-ray powder pattern of single phase samples of $Li_7[VN_4]$ contains reflections not allowed in $P\bar{4}3n$, but indicating the space group $Pa\bar{3}$. The single crystal investigation of the present study confirms this observation. Therefore, $Li_7[VN_4]$ is an isotype of both $Li_7[NbN_4]$ and $Li_7[TaN_4]$. Li and V are coordinated tetrahedrally by nitrogen. The distances $d$(Li—N) range from 2.029(9) Å to 2.200(7) Å; the distances $d$(V—N), 1.813(6) Å and 1.851(3) Å, are in good agreement with those from literature [3, 4, 5]. N is surrounded by seven Li and one V forming a distorted cube. All compounds of the formula type $Li_7[MN_4]$ (M = transition metal) crystallize in distorted $CaF_2$-type superstructures. M and Li occupy the F-site in an ordered manner, resulting in isolated tetrahedra $[MN_4]^{7-}$. The crystal structures of the group 5 and group 7 compounds differ in the relative arrangement of the metal ions. In both types of superstructures, the 18 neighboring tetrahedral holes in the *ccp* of nitrogen around the M sites are exclusively occupied by Li. Different arrangements of the M ions in the further surroundings lead to the different crystal structures for the group 5 and the group 7 compounds, respectively.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | black, cube, size 0.1 × 0.1 × 0.1 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| μ: | 20.75 cm$^{-1}$ |
| Diffractometer, scan mode: | Rigaku AFC7-CCD, 0° < ϕ < 360°, Δϕ = 0.5°, 60°-ω-scan at χ = 90°, Δω = 0.5° |
| $2\theta_{max}$: | 56.78° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 1186, 331 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 326 |
| $N(param)_{refined}$: | 37 |
| Programs: | SHELXL-97 [6], DIAMOND [7] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| V(1) | 8*c* | 0.36993(6) | *x* | *x* | 0.0032(4) | $U_{11}$ | $U_{11}$ | 0.0001(2) | $U_{12}$ | $U_{12}$ |
| N(1) | 8*c* | 0.2609(3) | *x* | *x* | 0.010(1) | $U_{11}$ | $U_{11}$ | 0.000(1) | $U_{12}$ | $U_{12}$ |
| N(2) | 24*d* | 0.4848(3) | 0.2597(3) | 0.4787(4) | 0.010(2) | 0.010(2) | 0.014(2) | 0.000(1) | 0.000(1) | −0.002(1) |
| Li(1) | 8*c* | 0.1344(7) | *x* | *x* | 0.015(2) | $U_{11}$ | $U_{11}$ | 0.006(3) | $U_{12}$ | $U_{12}$ |
| Li(2) | 24*d* | 0.1296(7) | 0.3845(7) | 0.1315(7) | 0.017(3) | 0.019(3) | 0.019(4) | −0.006(3) | 0.008(3) | −0.009(3) |
| Li(3) | 24*d* | 0.3632(7) | 0.3801(7) | 0.1041(7) | 0.018(3) | 0.018(3) | 0.014(3) | 0.007(3) | −0.014(3) | −0.007(3) |

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