High-pressure Synthesis and Preliminary X-Ray Investigation of a New Vanadium Fluoride Bronze, K$_x$VO$_3$F$_{3-x}$ (x = 0.25)

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Recently a series of vanadium oxide fluoride bronzes $M_xV_2O_5F_y$ ($M$ = Li and Na) have been reported and their structures compared with the corresponding vanadium oxide bronzes $M_xV_2O_5$. Systematic work is now in progress with the aim to prepare vanadium bronzes with the formula $M_xVO_{3x}F_{3-x}$ ($M$ = Na, K, Rb, and Cs). This is a preliminary note on a new potassium vanadium oxide fluoride with the composition K$_{4.25}$V(O,F)$_6$.

The starting materials were powdered potassium vanadate and vanadium trifluoride intimately mixed in a dry box in various ratios $x/(1-x)$ according to the formula:

$$xKVO_3 + (1-x)VF_3 \rightarrow K_xVO_{3x}F_{3-2x}$$

The syntheses were performed in sealed gold tubes at 700°C and 3 kb in an autoclave with argon as pressure medium.

In the range 0.25 $\leq x \leq$ 0.30 a single phase seemed to be present as judged from Guinier powder patterns. A small prismatic single crystal was isolated from a preparation with $x = 0.25$. Rotation and Weissenberg photographs ($hk0-hk4$) were taken with CuKα radiation and with the rotation axis in the prism axis ($c = 7.48$ Å). It was noticed that the layer lines with $l = 2n+1$ were extremely weak which implies that the heavy atoms must be situated in (or very close to) planes $c/2$ apart. Strongly exposed Weissenberg photographs ($l = 2n$) were indexed with the following hexagonal unit cell dimensions:

$$a = 29.39 \, \text{Å} \quad c = 7.48 \, \text{Å}$$

No conditions limiting possible reflections were observed. The Laue symmetry was found to be 6/m. Not considering the weak reflections, a sixteen times smaller sub-cell with the dimensions $a' = 7.35$ Å was recognized in the Weissenberg photographs. More accurate cell constants of the sub-cell were derived from a powder photograph taken with a Guinier camera, using CuKα radiation. All lines were indexed on the basis of a hexagonal cell, with the following edge lengths:

$$a' = 7.347 \pm 0.003 \, \text{Å} \quad c = 7.481 \pm 0.003 \, \text{Å}$$

The density of the sample was 3.27 g cm$^{-3}$, which corresponds to 96 formula units K$_{4.25}$VO$_{3.75}F_{2.45}$ in the true unit cell ($d_{calc} = 3.29$ g cm$^{-3}$).

The cell dimensions of the sub-cell suggest a structural relationship to the hexagonal tungsten bronze, K$_{4.25}$WO$_3$, studied by Magnéli. Preliminary calculations of the structure amplitudes have shown this assumption to be correct. A structural study is in progress.

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