High-pressure Synthesis and Preliminary X-Ray Investigation of a New Vanadium Fluoride Bronze, $K_xVO_{3x}F_{3-3x}$ ($x=0.25$)

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Recently [1-3] series of vanadium oxide fluoride bronzes $M_xV_2O_{5-y}F_y$ (M = Li and Na) have been reported and their structures compared with the corresponding vanadium oxide bronzes $M_xV_2O_5$.[4-6] Systematic work is now in progress with the aim to prepare vanadium bronzes with the formula $M_xVO_{3x}F_{3-3x}$ (M = Na, K, Rb, and Cs). This is a preliminary note on a new potassium vanadium oxide fluoride with the composition $K_{0.25}V(O,F)_3$.

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

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

The syntheses were performed in sealed gold tubes at 700°C and 3 kb in an autoclave with argon as pressure medium.[7]

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 crystal was isolated from a preparation with $x=0.25$. Rotation and Weissenberg photographs ($hk0-hk4$) were taken with Cu$K\alpha$ 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 Cu$K\alpha$ 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 $K_{0.25}VO_{0.75}F_{2.25}$ 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, $K_{0.27}WO_3$, studied by Magnéli.[8] Preliminary calculations of the structure amplitudes have shown this assumption to be correct. A structural study is in progress.

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