

BRIEF COMMUNICATION

A New Polymorph of VO₂ Prepared by Soft Chemical Methods

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A novel polymorph of VO₂, designated VO₂(C), has been prepared by dehydration of the new layered vanadium oxide hydrate, VO₂ · 1/2 H₂O. The hydrate is prepared in high yield as a single phase from the hydrothermal reaction of the hydrolyzate of VCl₄ and NaOH in a molar ratio of 1:4.5 for 96 hours at 200°C. The hydrate crystallizes in the tetragonal space group *I4/mmm*, with $a = 3.7211(6)$ Å, $c = 15.421(1)$ Å, $Z = 4$, and $R = 0.045$ as determined by X-ray single crystal diffraction. The structure consists of layers of VO₅ square pyramids, each of which shares its four basal edges with four neighboring VO₅ square pyramids. Water molecules that reside between the layers can be removed reversibly to give the new layered oxide VO₂(C). © 1998 Academic Press

The crystal chemistry of the binary vanadium oxides, VO_x, varies in oxygen compositions ranging from $x = 1$ to $x = 2.5$ and displays a wide variety of structure types (1). Several of these materials are technologically important with uses in oxidation catalysis (2) and battery applications (3). At $x = 1$, VO adopts a cubic rock salt structure which contains a high percentage of defects. The defects were revealed when Mathewson *et al.* observed a difference in the X-ray density 6.50 g/cm³ and the pycnometric determination of 5.6 g/cm³ (4). At $x = 1.5$ V₂O₃ adopts a structure similar to corundum (5). Asbrink *et al.* discovered the monoclinic crystalline phase V₃O₅ (6). Between the values $x = 1.75$ and 1.88 there exist the triclinic Magneli phases which have the general formula V_nO_{2n-1} ($4 \leq n \leq 8$) (7, 8). At $x = 2$, five different phases have been reported (8–13). The next set of important crystalline VO_x phases exist between $x = 2.17$ and 2.33 with the general formula V_nO_{2n+1} ($n = 3, 4, \text{ and } 6$) (14–17). Finally, the most oxygen-rich phase, V₂O₅, is well known and has been structurally characterized (18). Physical properties of the vanadium oxides vary, with electrical conductivity differing from metallic in some VO₂ polymorphs and V₂O₃ to semiconducting in V₂O₅.

Several polymorphs of VO₂ are known. A high temperature rutile VO₂ phase was crystallized in the space group *P4/mmm* (8). Anderson recognized the second VO₂ phase, which crystallizes monoclinic *P2₁/c* (9, 10), while a triclinic VO₂ phase fairly similar to Andersson's monoclinic phase has also been identified (11). These three VO₂ structures are similar and interconverted upon heating from 325 to 340 K. Two additional VO₂ phases previously reported are designated VO₂(A) and VO₂(B). The tetragonal VO₂(A) crystallizes in the space group *P4₂/nmc* (12) while the monoclinic VO₂(B), first characterized by Théobald *et al.*, crystallizes in space group *C2/m* (13). When viewed down the (110) direction, VO₂(A) exhibits two edge sharing octahedra which edge share with two additional octahedra to produce a layer of stair stepping octahedra. These layers are linked to each other at the protruding corners of each pair of octahedra to produce a three-dimensional framework. When viewed down the *c*-axis, VO₂(B) shows the same {VO₆} sheets as VO₂(A); however, these sheets of {VO₆} octahedra produce two distinct structures, based on the superpositions of the {VO₆} octahedral layers (12). VO₂(A) has been synthesized hydrothermally by heating a suspension of VO(OH)₂ to 250°C for 48 hr and by heating a suspension of V₂O₃ and V₂O₅ between 220 and 330°C (12). Similarly, VO₂(B) is prepared hydrothermally by heating a suspension of V₂O₃ and V₂O₅ to 220–150°C (19).

We report here the preparation of a new polymorph of VO₂ designated VO₂(C), (1), which is built up from O = VO_{4/4} layers and is prepared by dehydrating VO₂ · 1/2H₂O, (2). There was a recent claim of a compound “Li_xV_{2-δ}O_{4-δ}(H₂O)”, whose structure was determined from powder X-ray data, which crystallizes in the same space group and has essentially identical unit cell parameters to the title compound, VO₂ · 1/2H₂O, and an identical layer structure. The positions of the Li atoms were not precisely determined in this material. Curiously, the presence of the lithium cations in “Li_xV_{2-δ}O_{4-δ}(H₂O)” apparently does not distort the structure (20).

The hemihydrate is prepared by treating the hydrolyzate of VCl_4 with aqueous NaOH hydrothermally. Aquated " VO^{2+} " is prepared by very carefully adding VCl_4 dropwise to ice-cold water with stirring to give a solution 1.47 molar in vanadium (Caution: This reaction is violently exothermic and evolves large amounts of HCl ; the hydrolysis should be conducted in a fume hood with proper shielding). To 1.7 mL of this solution is added 3 mL of distilled H_2O and 4.5 mL of 2.5 molar NaOH . This mixture is sealed in a 23 mL polytetrafluoroethylene-lined stainless steel container and treated for 96 h at 200°C under autogeneous pressure (40% fill factor). The product, (2), is isolated as highly crystalline clumps of brown plates in 87% yield, and is single phase according to X-ray powder diffraction measurements. No superlattice duration due to ordering of the water molecules was observed.

The structure of the hemihydrate (2) was determined by X-ray single crystal diffraction (Table 1); it was shown to possess a layered structure. In (2) there are VO_2 layers alternating with layers of water molecules, as illustrated in Fig. 1, which is a projection down the $[100]$ crystallographic direction. The sites in which the water molecules reside are too close together to be fully occupied and, according to the X-ray refinement and TGA data, are only half occupied. The layers in (2) consist of layers of composition $\text{O}=\text{VO}_{4/4}$ built up from V-centered square pyramids (Fig. 2). The vanadyl $\text{V}=\text{O}$ groups are perpendicular to the plane of the layer with each vanadyl group pointing toward the opposite side of the plane as its four edge-sharing nearest neighbors (Fig. 1).

Dehydration of (2) is accomplished *in situ* by heating the sample at 200°C for 4 days under vacuum on a Scintag

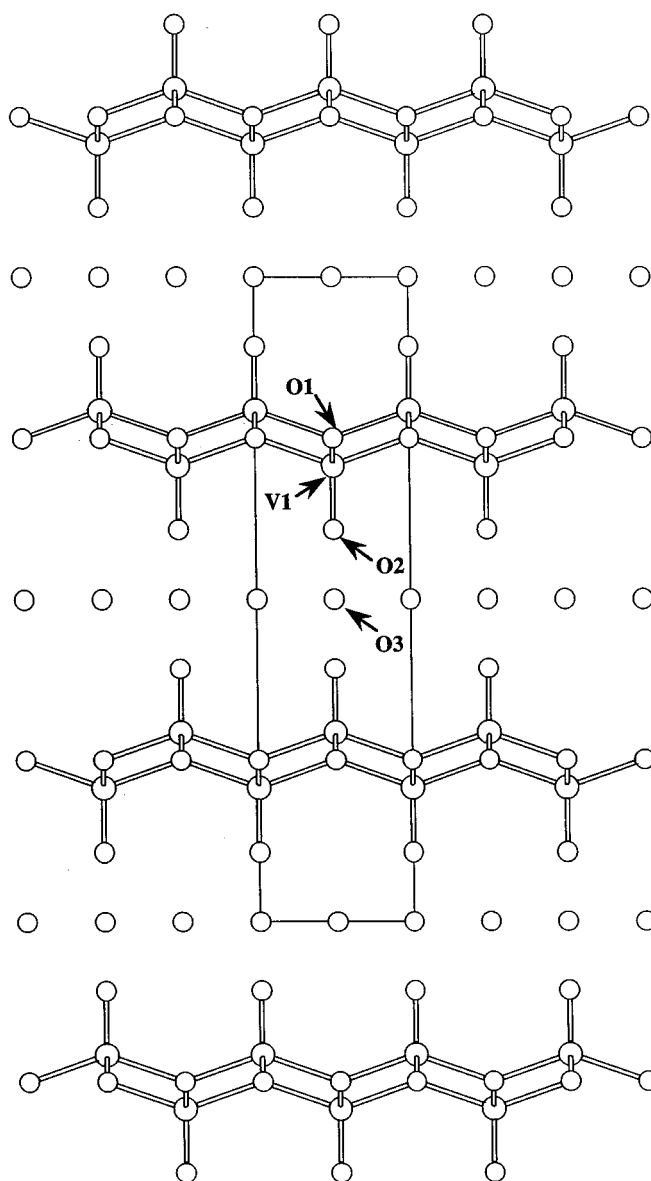


FIG. 1. A projection down the $[100]$ crystallographic direction showing the VO_2 layers alternating with layers of water molecules (water sites are half occupied), and the unit cell outline. Atom scheme: bridging oxo-group, O1; terminal oxo-group, O2; water oxygen, O3. Selected bond lengths (\AA) and angles ($^\circ$): $\text{V}-\text{O}1$, 1.9727(7) ($\times 4$); $\text{V}-\text{O}2$, 1.540(8) ($\times 1$); $\text{O}1-\text{V}-\text{O}1$, 141.18(7) and 83.66(2); $\text{O}1-\text{V}-\text{O}2$, 109.41(4). Valence sums: V, 4.33; O1, 2.23; O2, 2.06.

TABLE 1
Crystallographic Data for $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$

Empirical formula	$\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$
Formula weight	91.95
Crystal color, habit	black, plate
Crystal dimensions	$0.20 \times 0.05 \times 0.20$ mm
Crystal system	tetragonal
Lattice type	I-centered
Lattice parameters	$a = 3.7211(6)$ \AA $c = 15.421(1)$ \AA $V = 213.54(7)$ \AA^3
Space group	$I4/mmm$ ($\# 139$)
Z-value	4
D_{calc}	3.015 g/cm^3
$\mu(\text{MoK}\alpha)$	42.78 cm^{-1}
Diffractometer	Rigaku AFC7R
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$ \AA)
Temperature	20.0°C
No. of reflections measured	Total: 214 Unique: 172 ($R_{\text{int}} = 0.036$)
hkl range	0, 0, 0 to 5, 5, 20
Reflection/parameter ratio	13.67
Residuals: R ; R_w	0.045; 0.050

X-ray powder diffractometer equipped with a high-temperature stage, as confirmed by X-ray powder diffraction (Figs. 3, 4, and 5), to give the new VO_2 polymorph (1). The interlayer spacing observed for the (presumably) 001 reflection is consistent with the removal of most of the interlamellar water molecules. The fact that the layers found in hemihydrate (2) remain intact in $\text{VO}_2(\text{C})$ is firmly established by the observation that the X-ray powder diffraction

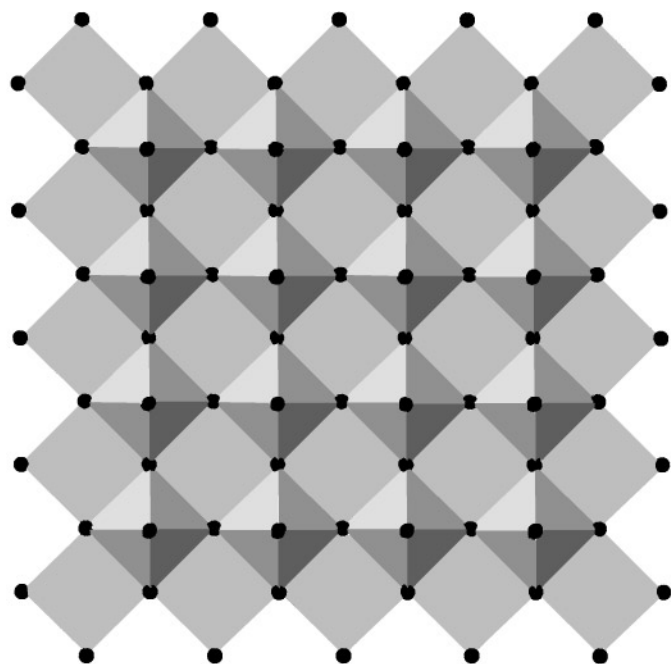


FIG. 2. A view perpendicular to the VO_2 layer in $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$. The vanadyl group of each VO_5 square pyramid points to the opposite side of the layer than its edge-sharing neighbors.

pattern of $\text{VO}_2(\text{C})$ is very rapidly replaced by that of the hydrate, in a highly crystalline form, upon exposure to water (Fig. 3). The powder diffraction data and the best DIFFaX fit are illustrated in Fig. 5, while Fig. 6 presents a schematic representations of the layer structure of $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$ and the DIFFaX model for the partially hydrated $\text{VO}_2(\text{C})$ sample. While the DIFFaX interpretation has been

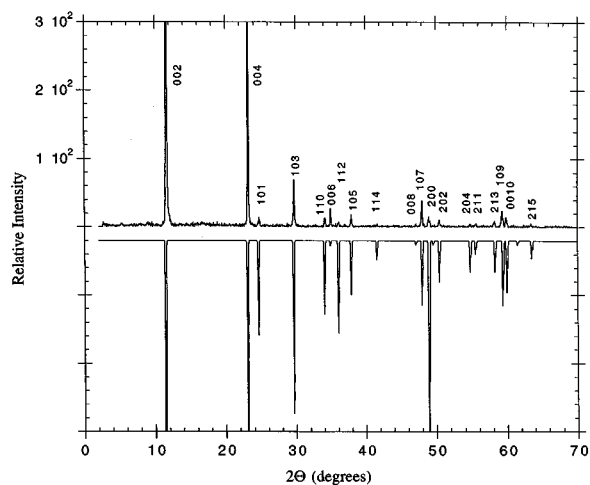


FIG. 3. Observed and calculated X-ray powder diffraction patterns for $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$ (I).

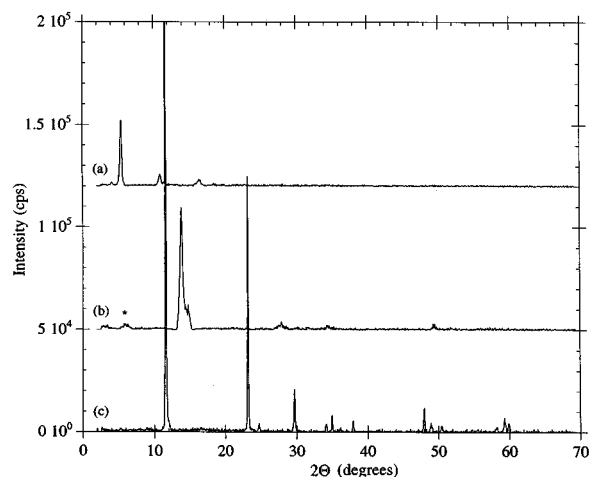


FIG. 4. X-ray powder diffraction patterns for (a) $\text{VO}_2(\text{C})$ intercalated with $\text{C}_4\text{H}_9\text{NH}_3\text{Cl}$, (b) $\text{VO}_2(\text{C})$, made by dehydrating $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$ (*indicates a peak due to the sample holder), and (c) $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$.

complicated by partial hydration of the extremely hydroscopic samples, a consistent model for the layer structure has been derived.

When projected down the b -axis as in Fig. 6a, the apices of the vanadium square pyramids of adjacent layers of $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$ point directly at each other. In contrast, in the partially hydrated $\text{VO}_2(\text{C})$, the layer repeat pattern is more complicated, as shown in Fig. 6b. For layer pairs such as AB and CD, the apices are still directed at each other, possibly because of relatively high water content between such layers. However, it is significant that the layers can no longer be presumed to be planar. The water molecules tend to anchor the layers in place at a spacing of $c/2$, but in regions devoid of water, the layers bend and move closer together. The layer pairs denoted BC shift by either $a/2$ or $b/2$. Consequently, the apical oxygen assume the role of the water molecules in the hydrated crystal, giving rise to a lateral shift. Atomic coordinates are given in Table 2.

While the DIFFaX fit to the data is adequate (Figs. 5 and 6), the match is not perfect because DIFFaX assumes flat layers, rather than the undulatory layers of the partially

TABLE 2
Atomic Coordinates and $B_{\text{iso}}/B_{\text{eq}}$

Atom	x	y	z	B_{eq}
V(1)	1.0000	0.0000	0.20749(9)	1.15(2)
O(1)	1.0000	0.5000	0.2500	0.80(5)
O(2)	1.0000	0.0000	0.1077(5)	2.54(9)
O(3)	0.5000	0.0000	0.0000	4.1(4)

Note. $B_{\text{eq}} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$.

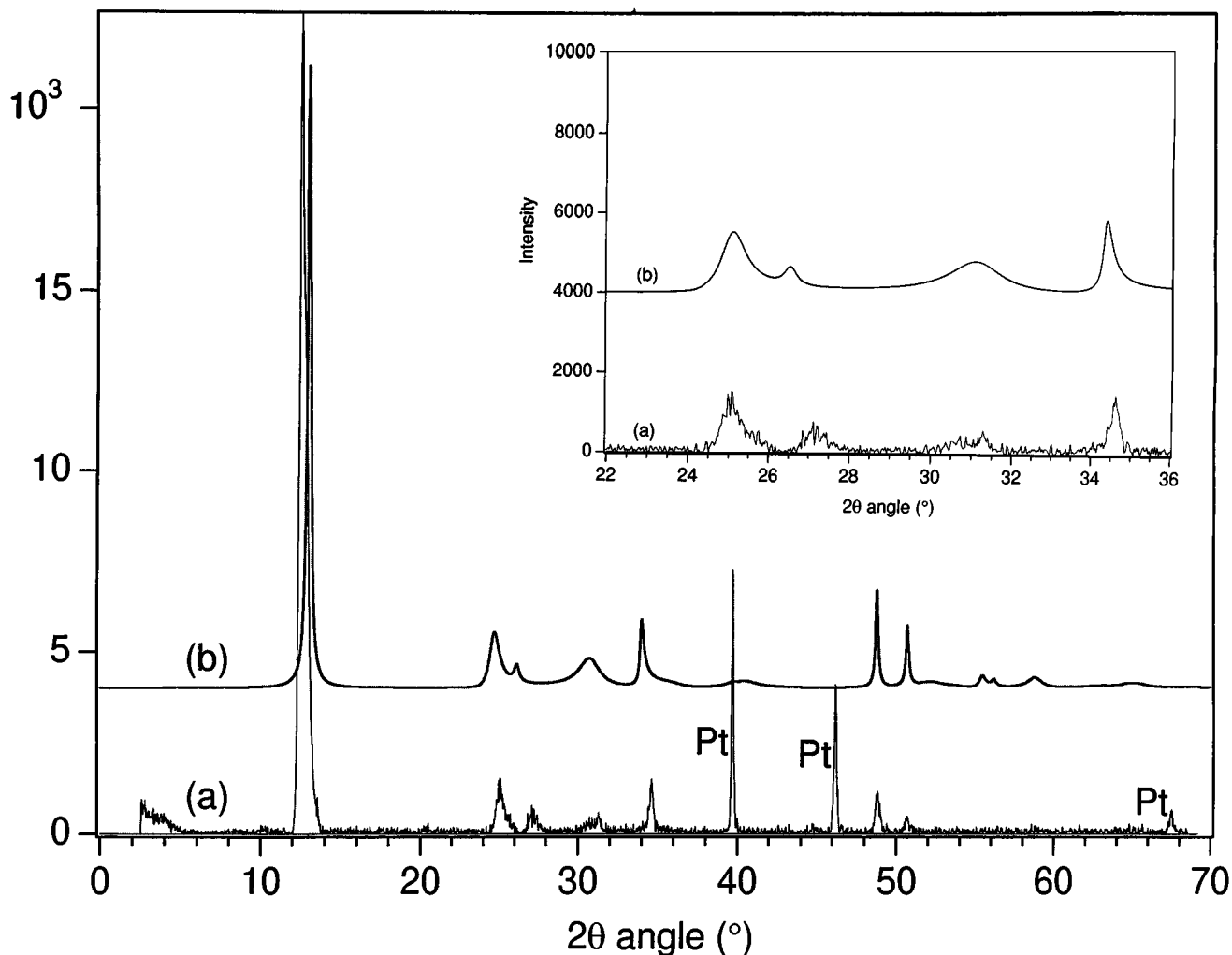


FIG. 5. X-ray powder diffraction pattern and DIFFaX simulation for partially hydrated $\text{VO}_2(\text{C})$. The peaks marked Pt result from the sample holder. A blowup of the 2θ range 22° – 36° , illustrating the DIFFaX fit to the data.

hydrated $\text{VO}_2(\text{C})$. Consequently, the average interlayer spacing depends on the average water content. This simulation assumes two interlayer spacings, $0.45c$ for the $(0, 0)$ shift (which occurs with 60% probability), and $0.43c$ for both the $(a/2, 0)$ and $(0, b/2)$ shifts (20% probability each). However, the high angle shoulder on the (002) reflection of $\text{VO}_2(\text{C})$ suggests a spread in the c -spacing of the partially hydrated material. The 2θ positions of the first intense peak (002) vary strongly with the extent of dehydration (compare Fig. 4b and Fig. 5a). Furthermore, the doubled 002 peak in Fig. 4b implies that not all crystallites in the sample dehydrate equally, factors which complicate DIFFaX simulations.

After heating under vacuum for 2 h at 400°C , the $\text{VO}_2(\text{C})$ sample converts to another crystalline phase, X, and further-

heating at 450°C for 40 h converts phase X to yet another crystalline material phase, Y. Phases X and Y are currently under investigation.

Preliminary experiments indicate that $\text{VO}_2(\text{C})$ will possess a diverse and extensive interlayer chemistry. For example, treatment with $n\text{-C}_4\text{H}_9\text{NH}_3\text{Cl}$ rapidly expands the basal spacing to 16.42 \AA , as shown in Fig. 4. Further details concerning the intercalation of $\text{VO}_2(\text{C})$ with a variety of species will be presented elsewhere shortly.

In summary, the hydrothermal treatment of the hydrolyzate of VCl_4 with base gives high yields of a new vanadium (IV) oxide, hemihydrate $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$. This hemihydrate is readily and reversibly dehydrated to a new VO_2 polymorph, $\text{VO}_2(\text{C})$, a sixth polymorph of VO_2 .

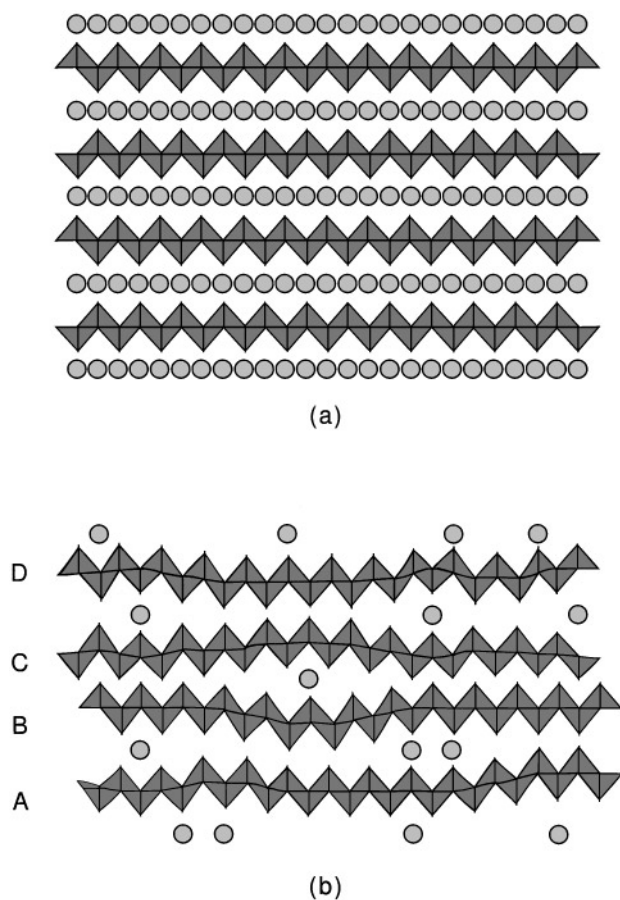


FIG. 6. (a) Schematic representation of the layer structure of $\text{VO}_2 \cdot 1/2\text{H}_2\text{O}$. The circles represent partially occupied water sites while the shaded triangles represent facets of the $\{\text{VO}_5\}$ square pyramids. (b) Schematic representation of the layer pattern of partially hydrated $\text{VO}_2(\text{C})$ from DIFFaX analysis.

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REFERENCES

1. J. Stringer, *J. Less-Common Met.* **8**, 1 (1965).
2. J. Miki, Y. Osada, T. Konoshi, Y. Tachibana, and T. Shikada, *Appl. Catal. A* **137**, 93 (1996).
3. W. Li, J. R. Dahn, and D. S. Wainwright, *Science* **264**, 1115 (1994).
4. C. H. Mathewson, E. Spire, and C. H. Samans, *Trans. Am. Soc. Steel Treating* **20**, 357 (1932).
5. R. E. Newnham and Y. M. de Haan, *Z. Kristallogr.* **117**, 235 (1962).
6. S. Asbrink, S. Friberg, A. Magneli, and G. Andersson, *Acta Chem. Scand.* **13**, 603 (1959).
7. H. Horiuchi, N. Morimoto, and M. Tokonami, *J. Solid State Chem.* **17**, 407 (1976).
8. G. Andersson, *Acta Chem. Scand.* **8**, 1599 (1954).
9. G. Andersson, *Acta Chem. Scand.* **10**, 623 (1956).
10. J. M. Longo and P. Kierkegaard, *Acta Chem. Scand.* **24**, 420 (1970).
11. T. Mitsuishi, *Japan J. Appl. Phys.* **6**, 1060 (1967).
12. Y. Oka, T. Yao, and N. Yamamoto, *J. Solid State Chem.* **86**, 116 (1990).
13. F. Théobald, R. Cabala, and J. Bernard, *J. Solid State Chem.* **17**, 431 (1976).
14. S. Andersson, J. Galy, and K. A. Wilhelmi, *Acta Chem. Scand.* **24**, 1473 (1970).
15. K. A. Wilhelmi and K. Waltersson, *Acta Chem. Scand.* **24**, 3409 (1970).
16. K. A. Wilhelmi, K. Waltersson, and L. Kihlborg, *Acta Chem. Scand.* **25**, 2675 (1971).
17. S. Horiuchi, M. Saeki, Y. Matsui, and F. Nagata, *Acta Crystallogr. Sect. A* **31**, 660 (1975).
18. H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Kristallogr.* **115**, 110 (1961).
19. F. Théobald, *J. Less-Common Met.* **53**, 55 (1977).
20. T. Chirayil, P. Zavalij, and M. S. Whittingham, *Solid State Ionics* **84**, 163 (1996).
21. M. M. J. Treacy, J. M. Newsam, and M. W. Deem, *Proc. R. Soc. London Ser. A* **433**, 499 (1991).