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LETTER TO THE EDITOR

Unit Cell Information for δ- and γ-$VOPO_4$

In a recent report by Kiely *et al.* (1), unit cell parameters for various polymorphs of $VOPO_4$ were tabulated. These phases are important because of their appearance in the various stages of formation and use of VPO catalyst employed in the air oxidation of butane to maleic anhydride. The presence of these phases has taken on renewed significance since the work of Coulston *et al.* (2) has conclusively demonstrated that V^{+5} species are crucial for the production of maleic anhydride. As a result, we have been investigating the δ and γ polymorphs of $VOPO_4$ with a combination of electron and synchrotron X-ray diffraction (XRD) techniques (3) in the hope of determining their crystal structures. While we have not yet succeeded in solving their structures, we here report that the unit cell parameters for δ- and γ-$VOPO_4$ listed by Kiely *et al.* (1) appear to be incorrect. To the best of our knowledge, these parameters first appeared in a review paper by Bordes (4). We also point out that the X-ray diffraction pattern of β'-$(VO)_2P_2O_7$ (5) is remarkably similar to that of δ-$VOPO_4$ (possibly with incomplete oxidation of vanadium to +5, i.e., $VOPO_{4-\delta}$) and that the unit cell parameters suggested for this phase should be viewed with caution.

The combination of electron and X-ray diffraction techniques has proven particularly valuable in probing the unit cells of the δ- and γ-$VOPO_4$ phases. A JEM-2000EX (at 200 kV accelerated voltage) microscope, equipped with Gatan 1024 × 1024 CCD camera, was used to obtain electron diffraction patterns on these two phases. The samples were directly deposited on conventional TEM grids. Inhouse X-ray diffraction patterns were obtained on a Philips APD-3720 powder X-ray diffractometer. High-resolution, X-ray powder diffraction patterns were obtained at the National Synchrotron Light Source, which is a DOE User Facility located at Brookhaven National Laboratory, Upton, NY. The samples were either mounted in capillaries to limit preferred orientation or prepared as flat-plate samples under nitrogen to maximize the diffraction intensities and to minimize hydration. Patterns were collected at beamlines X3b1 and X7a. In either case, a Si(111) monochromator, a Ge(200) analyzer, and slits on the order of 1 × 8 mm were used in conjunction with a scintillation counter to achieve the highest possible resolution and signal/noise ratio.

PREPARATION OF γ- AND δ-$VOPO_4$

(i) Precursor $VOHPO_4 \cdot 0.5H_2O$ was prepared according to Ref. (6). Briefly, this involves slurrying V_2O_5 in *i*-propanol/85% phosphoric acid under reflux for 24 h. The pale blue slurry is then filtered and the solid washed with acetone and suction dried.

(ii) δ-$VOPO_4$. Two grams of the blue precursor material $VOHPO_4 \cdot 0.5H_2O$ (6) was spread thinly in a quartz boat in a quartz-lined tube furnace. A flow of 100 ml/min dry oxygen was passed through the tube and exited through an oil bubbler to prevent moisture from contacting the sample. The sample was then ramped to 450°C over 7.5 h and held there for 7 days. The material became bright yellow during this heating and was then collected by sealing the tube, transferring to a nitrogen-filled glove-box, and bottling into a tightly capped vial. XRD of this material gave a pattern identical to that reported for the δ-phase of $VOPO_4$ (7). The sample is quite moisture sensitive and easily hydrates to the $VOPO_4 \cdot 2H_2O$ phase if exposed to humid air.

(iii) γ-$VOPO_4$. Following the same procedure as in (ii) above except that the precursor sample was ramped to 680°C over 6 h and held there for 4 h. The material became bright yellow during this heating. XRD of this material gave a pattern identical to that reported for the γ-phase of $VOPO_4$ (7) with some slight contamination from other (identified, and especially δ) $VOPO_4$ phases. The sample is also quite moisture sensitive and easily hydrates to the $VOPO_4 \cdot 2H_2O$ phase if exposed to humid air.

UNIT CELL OF δ-$VOPO_4$

Microcrystals of δ-$VOPO_4$ have plate-like shapes which yield sharp diffraction spots when an electron beam is focused perpendicular to the surface of the plates. A typical electron diffraction pattern is shown in Fig. 1. The 2-D unit cell in this projection has dimensions of about $d_{100} = 8.4$ and $d_{010} = 4.7$ Å with $\gamma^* = 90.0°$. Occasionally, some plates were tipped so that their surfaces were parallel to the electron beam, an orientation which permitted us to determine d_{001}. Figure 2 shows one such selected area electron diffraction pattern of a δ-$VOPO_4$ crystal in the [010] projection. The d_{001} value has thus been accurately measured to be 9.4 Å,

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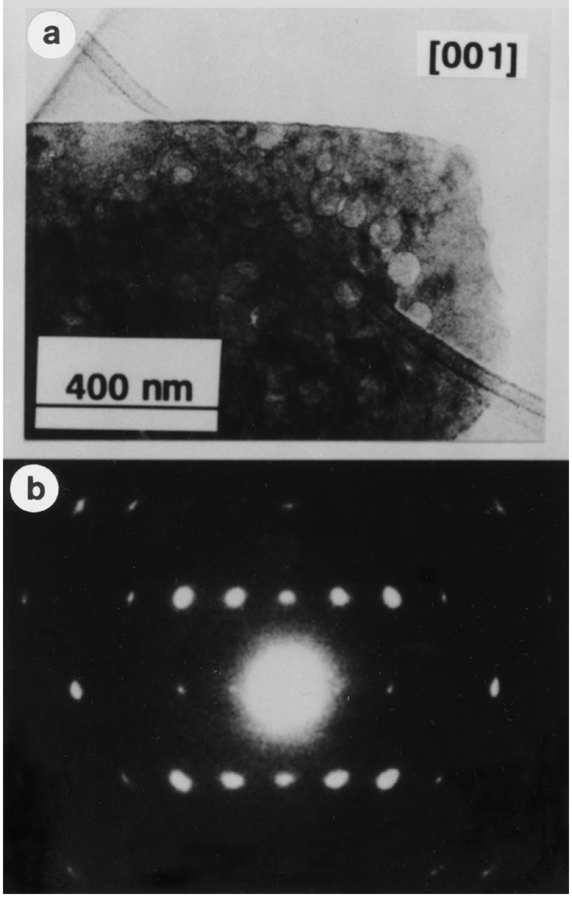

FIG. 1. Image (a) and selected electron diffraction pattern (b) of a typical plate-like δ-VOPO$_4$ crystal in [001] projection (electron beam perpendicular to the plate surface).

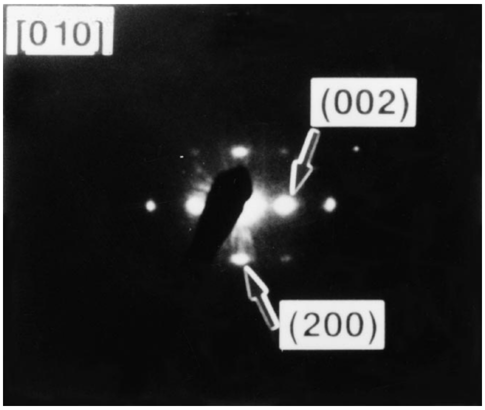

FIG. 2. Selected area electron diffraction pattern of δ-VOPO$_4$ crystals in [010] projection, electron beam parallel to the plate surface.

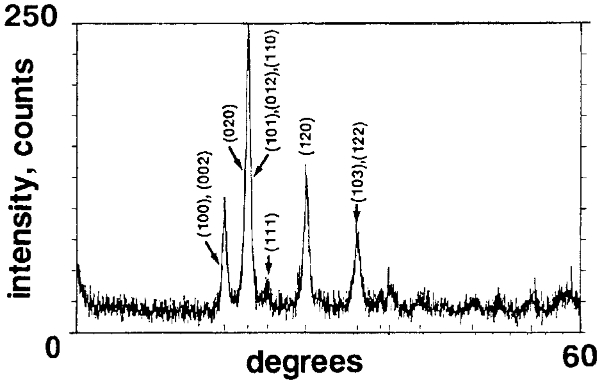

FIG. 3. Indexed X-ray diffraction pattern (Cu$K\alpha$) of δ-VOPO$_4$ based on the unit cell determined from the electron diffraction patterns and assuming orthorhombic symmetry.

using the unit cell d_{100} value as an internal standard. More precise values of the unit cell parameters can, in theory, be obtained by matching the repeat spacings found in the electron diffraction pattern with those found in the X-ray diffraction pattern. This match, however, is complicated by the broadness of the peaks in the X-ray pattern, a typical example of which is shown in Fig. 3. GSAS (8) refinements using a synchrotron diffraction pattern converged on a unit cell with $a = 8.50$, $b = 4.67$, $c = 9.46$ Å (assuming orthorhombic symmetry) when using the electron diffraction values as a starting point. However, a few weak diffraction spots in the higher angle region of the pattern were not fit by this cell. Furthermore, different starting parameters caused the refinement to converge on cells that were statistically different from the above values. Attempts to fit a monoclinic cell, i.e., with alpha shifted from 90°, fared no better. The basic problem is that it is difficult to refine a cell from a pattern which contains only a few broad peaks. Further complicating the situation is that the peaks in the X-ray diffraction pattern shifted noticeably when various attempts to produce "annealed" crystallites were attempted. Further work is continuing to understand the complexities of this phase, particularly with respect to the V oxidation state question, but it can certainly be said at this point that the historical unit cell ascribed to this phase is not correct.

UNIT CELL OF γ-VOPO$_4$

An electron diffraction pattern of γ-VOPO$_4$ close to the [010] projection is shown in Fig. 4. This suggests that $d_{100} = 4.9$, $d_{001} = 17.2$ Å, and $\beta^* = 90.0°$. The synchrotron powder diffraction pattern was subsequently obtained and the unit cell was indexed and refined using GSAS: orthorhombic, $a = 4.893$, $b = 8.800$, $c = 17.333$ Å (Fig. 5). The systematic extinctions, however, conformed to a monoclinic cell of space group $P2_1/c$, which suggests that the β angle is only approximately 90°. A refinement of the synchrotron data with a monoclinic cell starting from a β angle of 90.1° was not particularly stable but did suggest that some of the anisotropic peak broadening in this sample might be caused by a slight deviation of β from 90°. On cooling

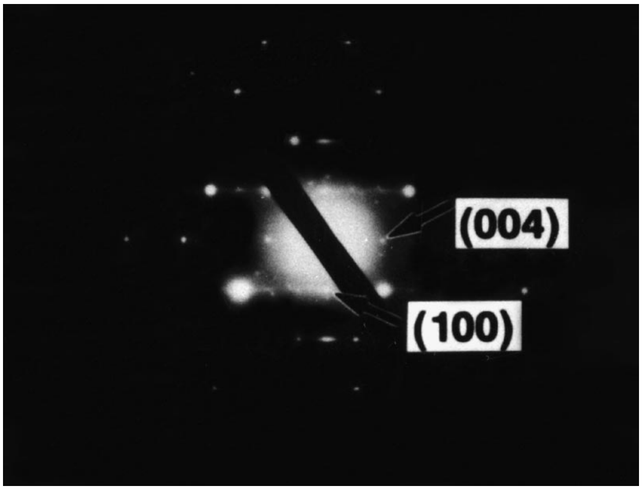

FIG. 4. Electron diffraction of single phase of γ-$VOPO_4$ close to [001] projection.

to 20 K, the high-angle peaks in the synchrotron pattern broadened considerably. One explanation is that the β angle had moved further away from 90° although no splitting, per se, was observed even at high angles. It is equally possible that a phase transition to a triclinic cell occurs at these low temperatures.

COMPARISON OF UNIT CELL PARAMETERS AND VOLUMES OF $VOPO_4$, $(VO)_2P_2O_7$, AND $(VO)_2P_2H_4O_9$

Table 1 compares the unit cell parameters and the volumes of δ-$VOPO_4$, γ-$VOPO_4$, $(VO)_2P_2O_7$, and $(VO)_2P_2H_4O_9$ (9, 10). They all have orthorhombic or nearly orthorhombic crystal symmetry. We also note that the in-plane values of the unit cell parameters for δ-$VOPO_4$, γ-$VOPO_4$, and $(VO)_2P_2O_7$ crystals are very similar, suggesting that they might have almost the same in-plane structure. The c values are quite different, possibly reflecting changes in the interlayer spacings from one crystal phase to another. Structural similarities of this type would make interphase changes rather easy and would lend support to the notion that these $VOPO_4$ phases could grow epitaxially on the $(VO)_2P_2O_7$ surface.

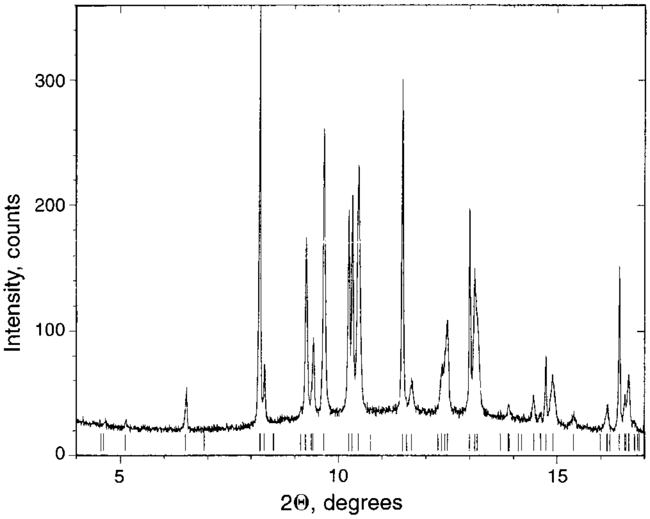

FIG. 5. Synchrotron X-ray powder diffraction pattern of γ-$VOPO_4$ crystals at a wavelength of 0.69928 Å. The tick marks indicate the positions of the Bragg reflections expected for an orthorhombic cell of dimensions $a = 4.893$, $b = 8.800$, $c = 17.333$ Å.

TABLE 1

Unit Cell Parameters and Volumes of δ-$VOPO_4$, γ-$VOPO_4$, $(VO)_2P_2O_7$, and $(VO)_2P_2H_4O_9$ Rearranged and Formulated to Accent Their Similarities

	In-plane dimensions (Å)		c (Å)	V (Å^3)
δ-$VOPO_4$	4.668	8.503	9.457	375.4
γ-$VOPO_4$	4.893	8.800	8.667 × 2	373.2 × 2
$(VO)_2P_2O_7$	4.792 × 2	8.291 × 2	7.729	407.1 × 4
$(VO)_2P_2H_4O_9$	9.592	7.416	5.689	404.7

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