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LETTER TO THE EDITOR

Comment on “Unit Cell Information for δ- and γ-$VOPO_4$” by Z. G. Li, R. L. Harlow, N. Herron III, H. S. Horowitz, and E. M. McCarron

In their letter, Li *et al.* (1) have presented possible reassignations of the unit cell parameters for the δ-$VOPO_4$ and γ-$VOPO_4$ phases. The new values differ very significantly from the “historical” unit cell parameters which were first deduced by Johnson *et al.* (2) and which have been referred to repeatedly in many subsequent publications (e.g., (3, 4) to name but a few). To date, no workers have been able to present a full structural determination (i.e., a full space group analysis with definite atomic coordinates) for these two phases. It is important that this latter goal be achieved since there is a growing body of evidence to suggest that these two $VOPO_4$ polymorphs play an active role in the VPO catalytic system.

The nature of the active phase in the VPO catalyst has been a matter of controversy for a number of years. Some researchers (5, 6) favour a single V^{4+} compound, $(VO)_2P_2O_7$, to be the active phase and have indicated that the presence of other phases may be a consequence of incomplete activation. The first definitive evidence for the active role of V^{5+} phases was gained from an *in situ* laser Raman spectroscopy (LRS) study of the activation of the $VOHPO_4 \cdot 0.5H_2O$ precursor by Hutchings *et al.* (7) in 1994. They found that maleic anhydride (MA) production was only detected once the features associated with α_{II}-, γ-, and δ-$VOPO_4$ were observed *in addition* to the signals characteristic of poorly crystallised $(VO)_2P_2O_7$. Since then, Sananes-Schultz *et al.* (8, 9) have been able to correlate the selectivity to MA production with the V^{5+}/V^{4+} ratio as measured by XPS, LRS, and ^{31}P NMR spin echo mapping on Co-doped VPO materials. More recently, Coulston *et al.* (10) have provided further compelling evidence from time-resolved *in situ* X-ray absorption spectroscopy studies indicating that V^{5+} species are crucial for the production of MA. A very plausible model is that the active VPO catalyst consists of domains of various $VOPO_4$ phases supported on the $(VO)_2P_2O_7$ surface. It is therefore essential that the full structures of the δ- and γ-$VOPO_4$ phases are fully elucidated.

In an attempt to resolve the apparent contradiction between the unit cell parameters for δ- and γ-$VOPO_4$, as presented by Johnson *et al.* (2) and Li *et al.* (1), we have (at Liverpool University) independently prepared fresh standards of these two phases. The preparation procedures followed were identical to those described by Ben Abdelouahab *et al.* (11). The XRD spectra for δ- and γ-$VOPO_4$ were then acquired under and N_2 atmosphere in order to prevent hydration to $VOPO_4 \cdot 2H_2O$. The analysis of our XRD data using both sets of unit cell parameters are presented below.

δ-$VOPO_4$

The “historical” unit cell for δ-$VOPO_4$ is orthorhombic with $a = 6.422$ Å, $b = 6.262$ Å, $c = 9.091$ Å (2). The new unit cell as proposed by Li *et al.* (1) is also orthorhombic but with $a = 8.50$ Å, $b = 4.67$ Å, $c = 9.46$ Å.

The XRD pattern which we obtained for the δ-$VOPO_4$ phase is presented in Fig. 1 and is very similar to that previously published by Ben Abdelouahab *et al.* (11). The experimentally determined lattice plane spacings are listed in Table 1. Also shown are the theoretical plane spacings and Miller indices based on the historical unit cell and the newly proposed unit cell. It is clear that *both* descriptions at least in terms of lattice plane spacings give very reasonable matches to the measured lattice spacings. It is not possible to compare our peak relative intensities (I/I_{max} ratios) with those expected from both model structures, since neither specify atomic coordinates.

γ-$VOPO_4$

The “historical” unit cell for γ-$VOPO_4$ is monoclinic and has parameters $a = 9.643$ Å, $b = 15.335$ Å, $c = 16.618$ Å, and $\beta = 93.04°$ (2). The new cell as proposed by Li *et al.* (1) is orthorhombic with $a = 4.893$ Å, $b = 8.800$ Å, $c = 17.333$ Å.

The XRD spectrum we obtained from the γ-$VOPO_4$ standard is also presented in Fig. 1. The experimentally determined lattice plane spacings are listed in Table 2. Comparison with the theoretical spacing lists from both unit cell models, as shown in Table 2, again gives quite a good match for *both* unit cell descriptions. The peak relative intensities are qualitatively similar to those published previously for the γ-$VOPO_4$ standard (11). Quantitative comparisons of peak intensities with theoretical predictions from the two model unit cells are once again unfeasible due to the lack of atomic coordinates (and hence reliable structure factor data).

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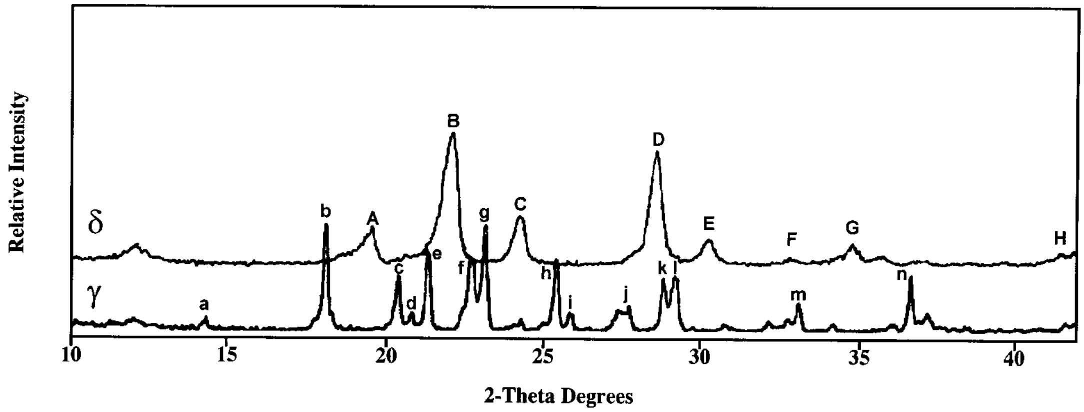

FIG. 1. XRD patterns from δ-$VOPO_4$ and γ-$VOPO_4$ standard phases prepared at Liverpool.

CONCLUDING REMARKS

It is apparent that both unit cell models for each of these $VOPO_4$ polymorphs are adequate, although not perfect, in describing their lattice plane spacings. The quantitative matching of peak intensities, which is required for a full structure determination, is, however, a much more difficult task since both systems are prone to (i) very strong texture effects due to their platelike nature and (ii) rapid hydration effects in ambient atmospheric conditions. A further complicating factor is that both standards (and in particular γ-$VOPO_4$) are almost impossible to prepare in pure "single" phase form.

The analysis of crystallography by electron diffraction methods as attempted by Li *et al.* (1) is also fraught with difficulties. For instance, hydration effects may occur between sample preparation and transferral into the electron microscope column. Furthermore, both phases are extremely sensitive to electron beam damage (4) and can be amorphised within a few seconds of observation. Selected area diffraction experiments, however, are useful in characterising features such as platelet normal directions, but are intrinsically far less accurate than XRD methods in determining absolute values of lattice plane spacings. In order to perform a full space group analysis on these phases in the electron microscope, it would be necessary to resort to the convergent beam electron diffraction (CBED) technique, which in this case is impractical because the samples would not withstand the high electron irradiation doses required.

On the basis of the evidence presented, it is difficult to unequivocally say which sets of lattice parameters are "correct." However, the reassignations proposed by Li *et al.* (1) do have considerable merit in that they highlight the structural similarity of δ- and γ-$VOPO_4$ with the $VOHPO_4 \cdot 0.5H_2O$ and $(VO)_2P_2O_7$ phases. Such similarities

TABLE 1

Analysis of XRD Data Using Both the Johnson (2) and Li (1) Parameters for δ-$VOPO_4$

		Johnson model		Li model	
Peak label	Experimentally determined spacing (Å)	Theoretical spacing (Å)	Index (*hkl*)	Theoretical spacing (Å)	Index (*hkl*)
A	4.6382	4.546	002	4.670	010
B	4.0661	4.021	111	4.093	110
C	3.6457	3.678	012	3.756	111
D	3.1401	3.131	020	3.143	210
E	2.9578	2.960	021	2.956	103
F	2.730	2.740	013	2.833	300
G	2.6097	2.578	022	2.617	212
H	2.1380	2.142	104	2.125	400

TABLE 2

Analysis of XRD Data Using Both the Johnson (2) and Li (1) Parameters for γ-$VOPO_4$

		Johnson model		Li model	
Peak label	Experimentally determined spacing (Å)	Theoretical spacing (Å)	Index (*hkl*)	Theoretical spacing (Å)	Index (*hkl*)
a	6.1426	6.127	102	6.175	012
b	4.8836	4.885	031	4.893	100
c	4.3351	4.352	032	4.333	004
d	4.2549	4.264	202	4.261	102
e	4.1430	4.147	004	4.152	111
f	3.9174	3.919	221	3.923	022
g	3.8299	3.833	040	3.835	112
h	3.4956	3.504	230	3.500	023
i	3.4353	3.449	213	3.437	113
j	3.2093	3.214	223	3.215	121
k	3.0890	3.087	105	3.087	024
l	3.0589	3.058	311	3.061	122
m	2.7026	2.721	016	2.723	025
n	2.4487	2.439	161	2.429	034

are intuitively expected because there is now considerable evidence to suggest that these phases can intertransform between structures in an epitaxial manner. For instance, it is well known that a loss of water of hydration from [001] $VOHPO_4 \cdot 0.5H_2O$ can lead to a *direct* topotactic transformation to [100] $(VO)_2P_2O_7$ (3, 4). More recently, however, it has also been demonstrated that the transformation from the hemihydrate to $(VO)_2P_2O_7$ can proceed through an *indirect* route via epitaxially related δ- and α_{II}-$VOPO_4$ phases (12–14). A detailed crystallographic understanding of these latter transformations is at present far from complete. It is envisaged, however, that a reassignation of the unit cells of δ- and γ-$VOPO_4$ into a frame of reference which is structurally (and intuitively) similar to $VOHPO_4 \cdot 0.5H_2O$ and $(VO)_2P_2O_7$ will be a welcome advance in enabling a more complete understanding of possible epitaxial transformations in this materials system. Presenting the $VOPO_4$ phases in this manner will also make it easier to predict possible epitaxial orientation relationships between δ- and γ-$VOPO_4$ "domains" supported on various $(VO)_2P_2O_7$ surfaces.

In conclusion, we believe that the new work presented by Li *et al.* (1) is a welcome step in the right direction towards the goal of providing a full description of the unit cell structures for δ- and γ-$VOPO_4$.

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