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The crystal structure of ε-$VOPO_4$

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This work is dedicated to Prof. Dr. Hans Georg von Schnering on the occasion of his 75th birthday

Abstract

The crystal structure of ε-$VOPO_4$ was determined in the space group *Cc* from X-ray powder diffraction data using a rigid body approach. The resulting structure is compared to a recently published, slightly different structure model (space group $P2_1/n$) using Rietveld refinement. It was found that the new *Cc* model consistently yields a better fit to the observed data and exhibits a less distorted, more stable geometry. The crystal structure of ε-$VOPO_4$ is discussed in comparison to β-$VOPO_4$, monoclinic $VPO_4{\cdot}H_2O$, and other related structures.

Keywords: Vanadium; Phosphate; Crystal structure; Powder diffraction; Ab initio structure determination; Rigid body constraints

1. Introduction

The numerous polymorphs of $VOPO_4$ have attracted much attention among both catalysis researchers and electrochemists. The phases α_{II}-, δ- and γ-$VOPO_4$ have been reported to be present in activated $(VO)_2P_2O_7$ catalysts for the partial oxidation of *n*-butane to maleic anhydride [1,2]. Thus, they may be related to the activity of the catalyst [3]. In lithium battery research, δ- and especially ε-$VOPO_4$, the most recently discovered polymorph [4], show promising electrochemical properties [5–8]. In both fields of research, knowledge of the crystal structure of the respective phases is desirable, since it is a prerequisite to uncover structure-(re)activity relationships. Despite all efforts reflecting this interest, the knowledge about the structures of several $VOPO_4$ polymorphs is still limited. The main reason is that many of the polymorphs are difficult to synthesize as single phase materials of reasonable crystallinity, combined with the inherent problems of crystal structure solution from powder diffraction data.

Since the discovery of ε-$VOPO_4$ by Lim et al., it was argued that its structure should be both similar to β-$VOPO_4$ [9], the most stable polymorph, and related to monoclinic $VPO_4{\cdot}H_2O$ [10], which can be reversibly converted to ε-$VOPO_4$ [4]. This claim was further substantiated by recent work of Song et al., where a structure model derived from monoclinic $VPO_4{\cdot}H_2O$ (space group $C2/c$) was refined successfully in the space group $P2_1/n$ [8].

While investigating the potential of a rigid body approach in ab initio structure determination from powder diffraction data for some of the $VOPO_4$ polymorphs, we found a slightly different model (space group *Cc*) for the structure of ε-$VOPO_4$, which will be presented here.

2. Experimental

2.1. Sample preparation

Monoclinic $VPO_4{\cdot}H_2O$ was prepared by the reduction of $VOHPO_4{\cdot}0.5H_2O$ (2.0 g) derived from the standard VPO route [11] with 1-octanol (40 ml) in an autoclave at 250 °C for 24 h

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in N_2. The precursor was recovered by filtration, washed with acetone, and dried at 110 °C in air for 24 h. The ε-$VOPO_4$ was prepared by calcination of the as synthesized monoclinic $VPO_4{\cdot}H_2O$ at 500 °C for 4 h in air.

2.2. Diffraction data collection

X-ray diffraction data were collected on a D8 ADVANCE powder diffractometer (Bruker AXS) in Theta/Theta reflection geometry. Cu K_α radiation from a Cu X-ray tube was selected secondarily by means of a SolX energy dispersive solid state detector (Baltic Instruments). The data acquisition was performed in six consecutive scans. After confirming that the diffraction pattern exhibited no change over the total acquisition time of 33 hours, the six data sets were averaged.

2.3. Structure determination

The program Topas [12] was used for ab initio structure determination from powder diffraction data (SDPD). In a first step, a whole powder pattern decomposition (WPPD) was performed employing the Le Bail method. However, the purpose of this procedure was not to extract *hkl* intensities, but to obtain reasonable background, profile, and lattice parameters. Since the diffraction data can be equally well explained using either a monoclinic or orthorhombic unit cell, both possibilities were tested separately. The starting lattice parameters were taken from reference [4]. As the correct space group was unknown, space groups without any systematic absences were chosen for the WPPD ($P2/m$ for the monoclinic and *Pmmm* for the orthorhombic cell, respectively).

In a second step, the actual SPDP process was performed in direct space on the diffraction step intensity data [13], using fixed parameters obtained from previous refinement in the WPPD. To increase the chance of a successful structure solution, a rigid body approach was employed, i.e., the internal geometries of an idealized tetrahedral PO_4 group and a linear V=O fragment were kept fixed during the process, with bond lengths derived from the known crystal structure of β-$VOPO_4$ (ICSD entry 9413) [9]. Only the translation and rotation of these two rigid bodies were subject to randomization and refinement in the simulated annealing process. A number of monoclinic and orthorhombic space groups were tested by trial and error. Space groups with systematic absences incompatible with the diffraction pattern were excluded a priori, as were some candidates that seemed geometrically unlikely (e.g., orthorhombic space groups with intersecting mirror planes). The results were evaluated according to both the R_{wp} value and the plausibility of the resulting structure.

2.4. Structure refinement

All subsequent Rietveld structure refinements were also performed using the program Topas. In all cases, a common isotropic temperature factor was refined for all atoms. The presence of some β-$VOPO_4$ was taken into account by adding this phase to the refinement (fixed atomic coordinates, lattice parameters refined, common isotropic temperature factor shared with ε-$VOPO_4$). To avoid floating origin problems in the space group *Cc*, the x and z coordinates of the V atom were fixed to arbitrary values ($x = z = 1/2$). All bond lengths and angles were calculated with Platon for Windows [14,15]. Structure drawings were created with Diamond [16].

3. Results

3.1. Structure determination

The XRD data revealed that the sample used was not a single-phase material. In addition to the diffraction pattern of ε-$VOPO_4$, weak diffraction peaks typical for β-$VOPO_4$ were observed, as well as a very weak unidentified peak at 21.23° 2θ. The intensities of the impurity reflections overlapping with ε-$VOPO_4$ peaks were assumed to be weak enough to be ignored in the initial structure solution step.

Among all the space groups tested in the structure solution attempts, only the space group *Cc* yielded a plausible structure model, which was also the solution with the lowest R_{wp} value. This result confirms that the symmetry of the structure is indeed monoclinic, although the a and c lattice parameters are equal within a few standard deviations, rendering the unit cell pseudo-orthorhombic metrically. This situation results in a systematic overlap of *hkl* and *lkh* reflections, which severely reduces the data resolution and decreases the stability of the structure refinement, as was already indicated by Song et al. [8].

3.2. Structure refinement

To avoid stability problems, the refinement process was performed step-by-step, gradually increasing the number of free parameters. Thus, the rigid body constraints used in the structure solution process were first kept. After convergence, it was found that most atoms (i.e., the V=O fragment and an O–P–O part of the PO_4 unit) aligned very well in a common plane that corresponds to the mirror plane in the structure of β-$VOPO_4$. This "pseudo-mirror" like arrangement readily explains why the a and c lattice parameters of the monoclinic cell are so similar to each other, despite the absence of a higher (orthorhombic) symmetry. Based on this observation, the rather restrictive rigid body model was exchanged for a more flexible "pseudo-mirror model". The following constraints were used:

(i) lattice parameters a and c are equal,
(ii) above mentioned atoms lie exactly in one plane (the pseudo-mirror plane) by correlation of their z to their x coordinates, and
(iii) the remaining two oxygen atoms are pseudo-mirror images of each other, i.e., their x and z coordinates are cross-correlated while their y coordinates are equal.

After convergence, the pseudo-mirror constraints on the atomic coordinates were removed, followed by the $a = c$ constraint in the next step. Fig. 1 shows a plot of the final Rietveld