New Contributions to the Structural Chemistry of Vanadyl Orthophosphate VOPO₄

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The Crystal Structure of ε-VOPO₄ [1]

Background

ε-VOPO₄ is the most recently described polymorph of VOPO₄ [2]. Based on the chemical behavior and similarities in the X-ray diffraction patterns, it was proposed that the structure of ε-VOPO₄ should be both related to monoclinic VPO₄·H₂O and similar to β-VOPO₄. A Rietveld refinement of the monoclinic VPO₄·H₂O structure (space group C2/c) to the ε-VOPO₄ data was only of limited success [2]. Recently, a structure model derived from monoclinic VPO₄·H₂O was successfully refined in the lower symmetry space group $P2_1/n$ [3].

Experimental

Samples of ε-VOPO₄ were prepared at Cardiff University in the course of searching for potential VPO catalyst precursors by means of hydrothermal synthesis [4]. The X-ray diffraction pattern was subjected to ab initio structure solution attempts in various monoclinic and orthorhombic space groups using the TOPAS [5] software, employing a rigid body approach [1].

Results

The crystal structure of ε-VOPO₄ was successfully solved and refined in the monoclinic space group Cc (a = 7.266 Å, b = 6.893 Å, c = 7.265 Å, β = 115.34°; because $a \approx c$, the unit cell is pseudo-orthorhombic). This solution was found to be in better agreement with the experimental data than the previously published $P2_1/n$ model. Both models differ in the general orientation of the VO₅ pyramids. While the direction of pyramid stacks would alternate in the centrosymmetric space group $P2_1/n$ (Fig. 1, right), they all point into the same general direction in the acentric space group Cc (Fig. 1, left).
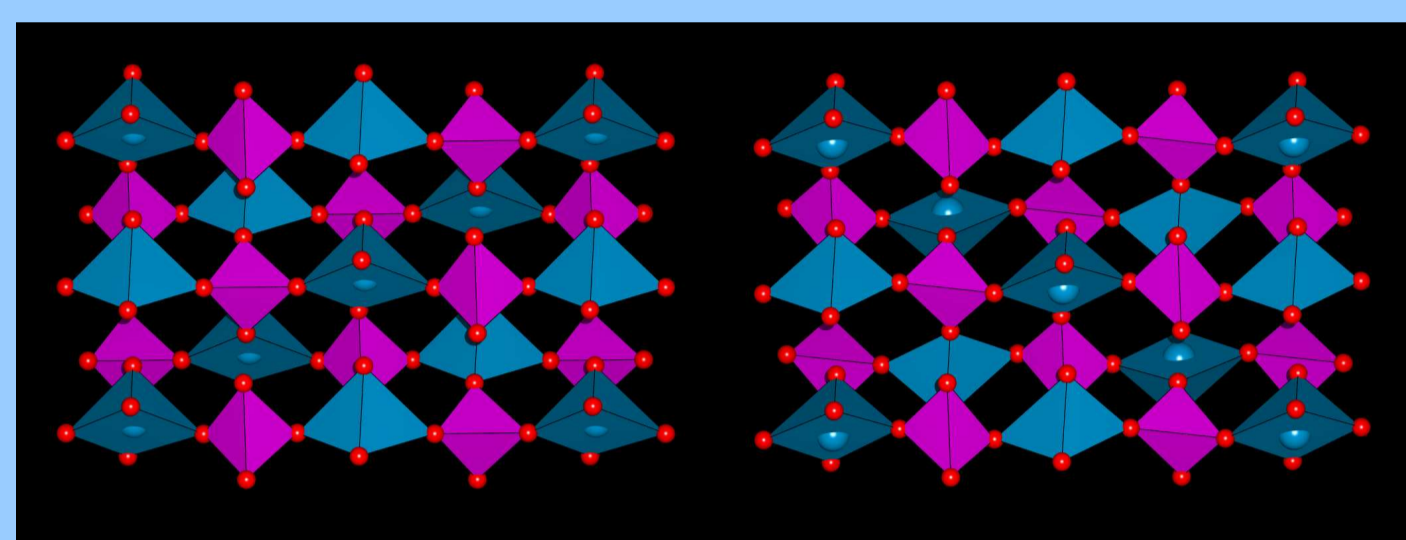
Fig. 1: Pyramidal representation of two structure models for ε-VOPO₄ in the space groups Cc (this work, left) and $P2_1/n$ (after reference [3], right), respectively.

The Crystal Structure of δ-VOPO₄ [6]

Background

δ-VOPO₄ was described in 1985 by Bordes and Courtine [7] as one of the minority phases found in activated (VO)₂P₂O₇ catalysts for the selective oxidation of n-butane to maleic anhydride. Since then, several unit cells and two structure hypotheses ("Bordes model" [8] and "Benabdelouahab model" [9, 10]) have been proposed. The reason for this uncertainty is that the material obtained is usually badly crystallized and often contaminated with other phases, yielding a diffraction pattern with rather broad, overlapping peaks. Only recently, well crystallized single phase material was obtained and investigated by means of TEM and powder XRD [11]. The diffraction pattern proved to be incompatible with the unit cells proposed until then, resulting in a new unit cell proposal of orthorhombic symmetry. Despite the high quality of the diffraction pattern, the crystal structure of δ-VOPO₄ could not be determined at that time.

Experimental

The preparation of well crystallized δ-VOPO₄ and the collection of the corresponding X-ray diffraction pattern were conducted at the former ACA Berlin (now Berlin branch of the Leibniz Institute for Catalysis at University Rostock), as previously published [11]. The structure solution described here is based on a re-investigation of aforementioned diffraction data. The program TOPAS [5] was used for all steps of the ab initio structure determination and subsequent refinement.

Results

A Le Bail pattern decomposition proved that the δ-VOPO₄ unit cell could be equally well described as tetragonal instead of orthorhombic. Thus, the higher (tetragonal) symmetry was assumed to be more probable. Structure solution attempts in various tetragonal space groups yielded an initial structure model in the space group $P4_2bc$, which was subsequently transferred into the higher symmetry space group $P4_2/mbc$ and refined. The obtained crystal structure of δ-VOPO₄ is found to be very similar to that of ω-VOPO₄, thus disproving both traditional structure hypotheses. The unit cell of δ-VOPO₄ (a = 9.055 Å, c = 8.608 Å) corresponds to a quadruple (2×2×1) unit cell of ω-VOPO₄ (see below).

The Polymorphs of VOPO₄ – Structural Systematics

Introduction

Seven polymorphs of VOPO₄ have been described so far: α_I, α_{II}, β, γ, δ, ε, and ω. With the work presented here, only the crystal structure of γ-VOPO₄ remains unknown. Now that six of seven polymorphs are characterized in sufficient detail, the general structure building principles of VOPO₄ can be discussed systematically.

Common features

All structurally characterized polymorphs of VOPO₄ share some common characteristics:

▪ Each vanadium atom is surrounded by six oxygen atoms with
 • one particularly short distance (vanadyl bond V=O),
 • four medium distances (V–O bonds to phosphate groups),
 • one rather long distance (V···O contact to next vanadyl group).
▪ V···O is always trans-positioned to V=O.
▪ Depending on whether V···O is considered a bond or not, the coordination geometry of vanadium can be described as a distorted VO₆ octahedron (⇒ "octahedral representation") or a VO₅ pyramid (⇒ "pyramidal representation"), respectively.
▪ Each VO₆ octahedron shares two trans-positioned corners with two other octahedra, forming infinite chains with [V=O···V=O···]∞ backbone.
▪ Each VO₆ octahedron shares four corners with four different PO₄ tetrahedra.
▪ Each PO₄ tetrahedron shares corners with four different VO₆ octahedra.

Distinguishing and grouping characters

The polymorphs of VOPO₄ can be characterized and grouped into three **structure families** according to the following characters:

▪ Three-dimensional arrangement of VO₆ chains (parallel only vs. parallel & perpendicular).
▪ Number of different VO₆ chains linked by a single PO₄ tetrahedron (3 vs. 4).
▪ Dimensionality of structure network in pyramidal representation (2D vs. 3D).

Further distinguishing (but non-grouping) characters:

▪ Relative directionality of adjacent chains (parallel vs. anti-parallel).
▪ Shape of [V=O···V=O···]∞ backbone (straight vs. zigzag).

	α family		β family		δ family	
	α_I	α_{II}	β	ε	δ	ω
▶ Relative chain arrangement	parallel only		parallel only		parallel & perpendicular	
▶ No. of chains linked by PO₄	4		3		4	
▶ Dimensionality (pyramidal view)	2D		3D		3D	
Chain directionality	anti-parallel	anti-parallel	anti-parallel	parallel	anti-parallel	(disordered)
Chain shape	straight	straight	zigzag	zigzag	zigzag	straight

One important additional property (which cannot be coded by simple characters) is the connectivity pattern, i.e. the possibility of different "stacking" of otherwise equivalent building blocks ⇒ distinction of **sub-families** (ε vs. β).
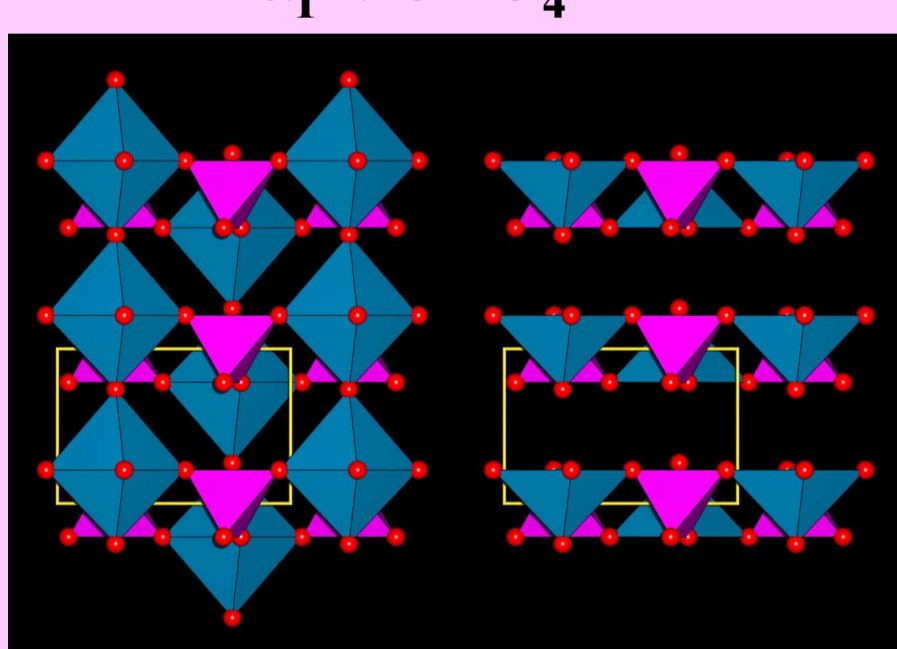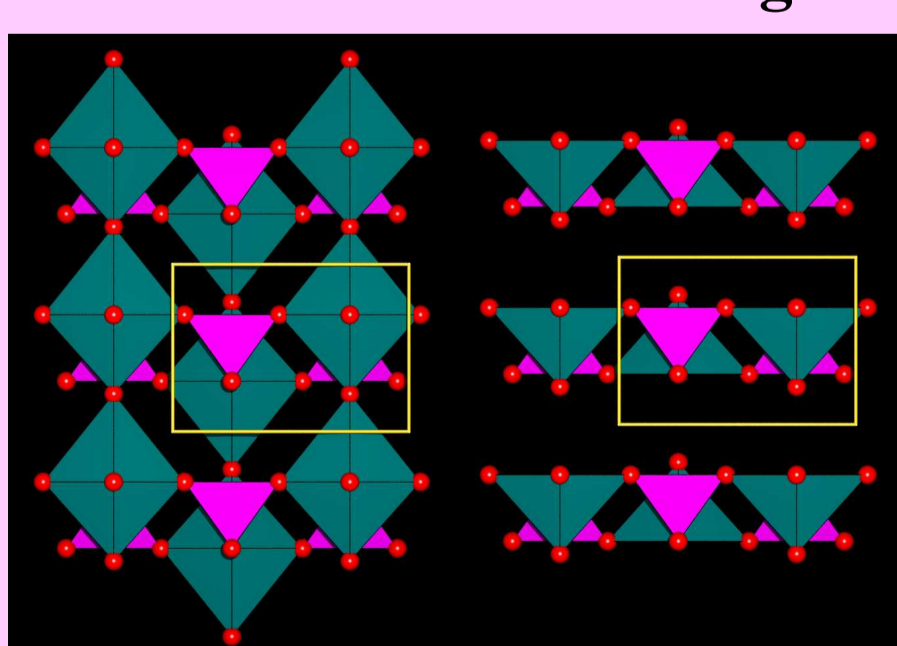
α structure family

α_I-VOPO₄ [12]

View along a axis in octahedral (left) and pyramidal representation (right).

α_{II}-VOPO₄ [13]
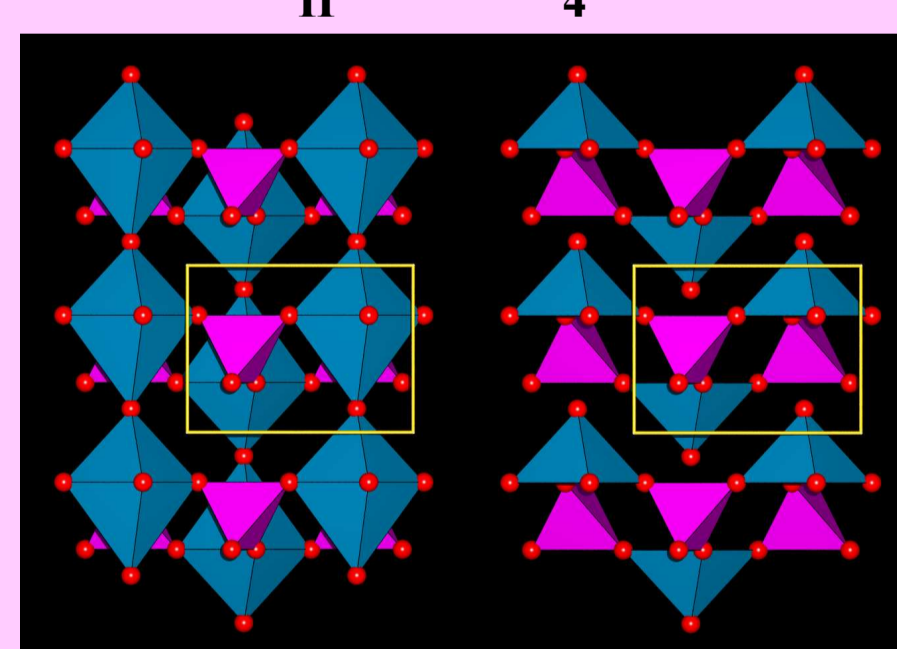
View along a axis in octahedral (left) and pyramidal representation (right).

related structures:

tetragonal LiVOPO₄ [14]

View along a axis in octahedral (left) and pyramidal representation (right). Li atoms omitted for clarity.

Same [VOPO₄] host lattice structure as in α_I-VOPO₄, but can be obtained from both α_I- and α_{II}-VOPO₄ by lithiation.

VOPO₄·2H₂O [15]

View along a axis in octahedral (left) and pyramidal representation (right).

Of the two water molecules per formula unit, one is coordinating to vanadium (oxygen atom shown), while the second one is crystal water (omitted for clarity).

Same [VOPO₄] host lattice structure as in α_I-VOPO₄, but can be obtained from both α_I- and α_{II}-VOPO₄ by hydration.
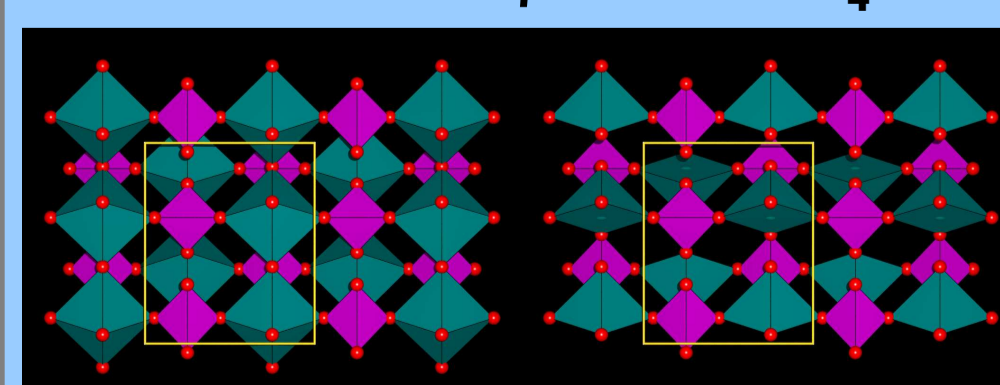
Remark:
The layered α-VOPO₄ structures show a rich intercalation chemistry with organic donor molecules (especially amides) instead of water.

β structure family

β sub-family
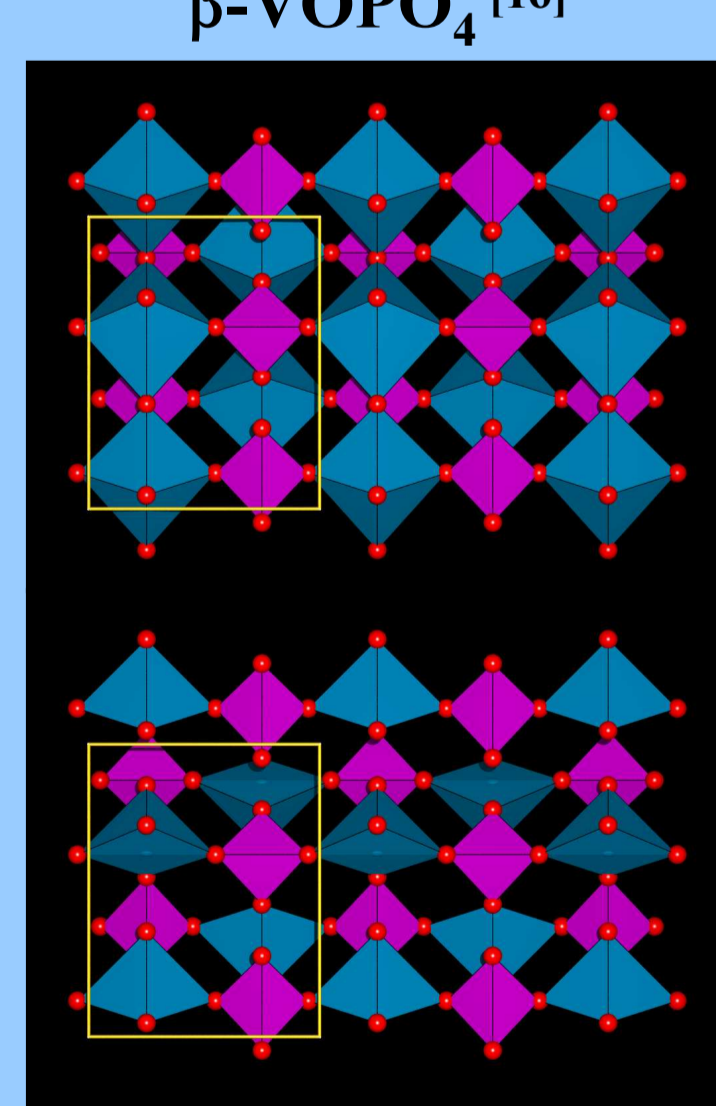
β-VOPO₄ [16]

Octahedral (top) and pyramidal representation (bottom).

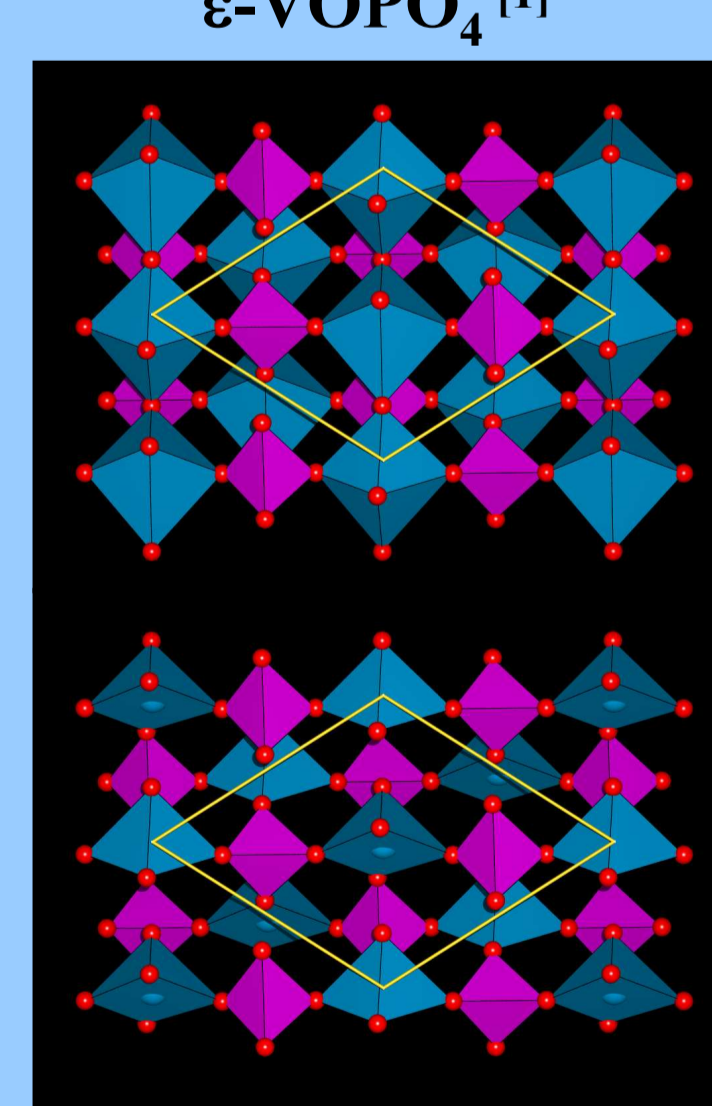### related structures:

orthorhombic β-LiVOPO₄ [17]

Octahedral (left) and pyramidal representation (right). Li atoms omitted for clarity.

VOHPO₄ [18]

Same space group and [VOPO₄] host lattice structure as β-VOPO₄ and β-LiVOPO₄ (no picture).

"New phase" of Lim et al. [2] ?

Crystal structure unknown. Prepared by (topotactic?) hydrogen-spillover reduction from β-VOPO₄ [2]. Could be a new polymorph of VPO₄·H₂O with the same connectivity as β-VOPO₄.

ε sub-family

ε-VOPO₄ [1]

Octahedral (top) and pyramidal representation (bottom).

related structures:
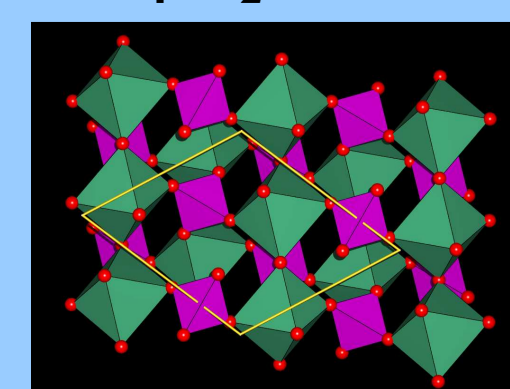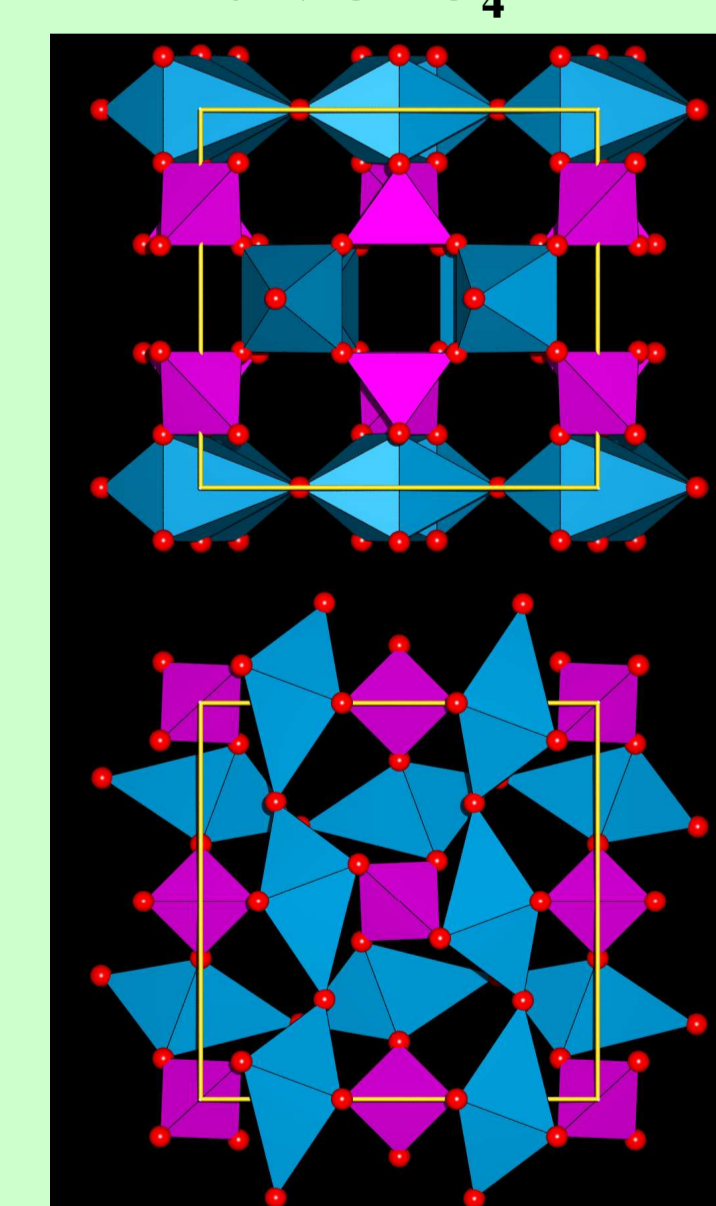
triclinic α-LiVOPO₄ [19]
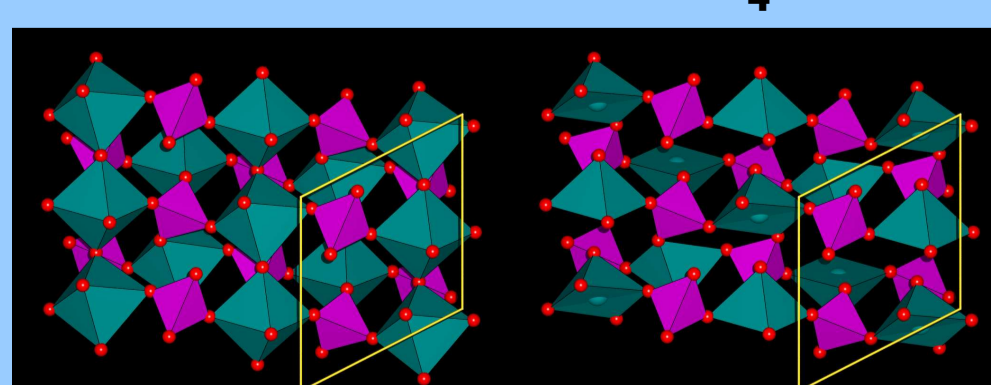
Octahedral (left) and pyramidal representation (right). Li atoms omitted for clarity.
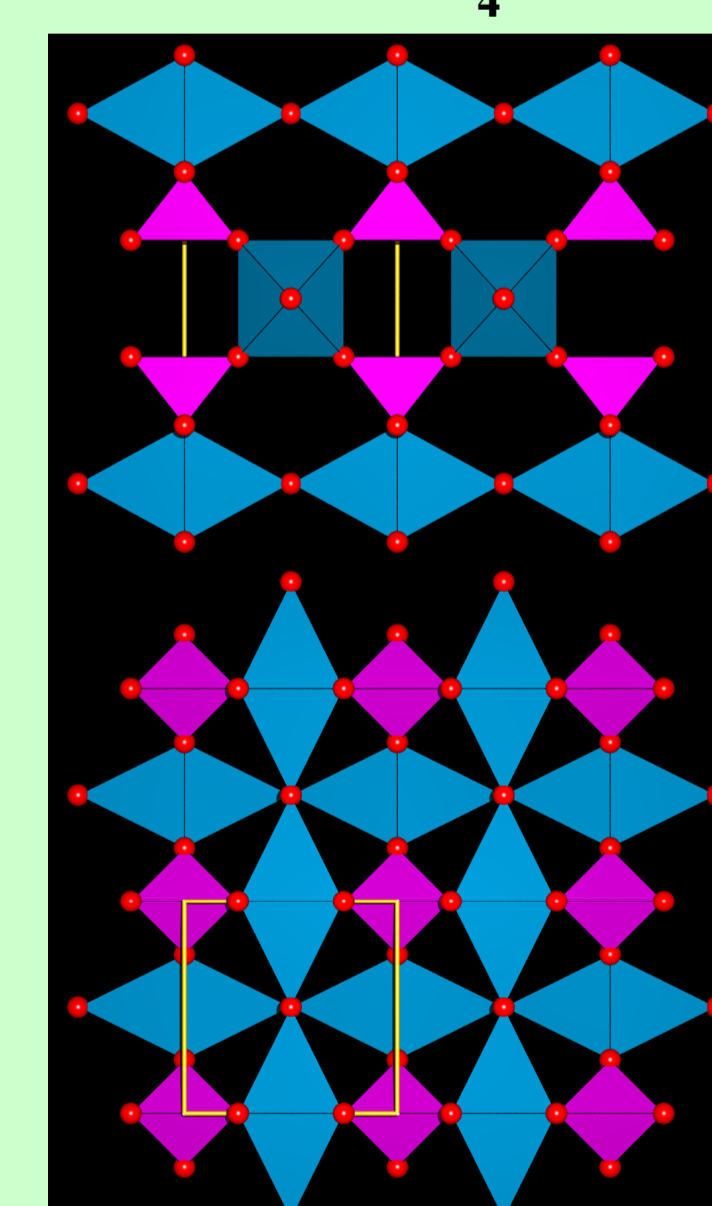
NaVOPO₄ [20, 21]

Monoclinic. Same [VOPO₄] host lattice structure as α-LiVOPO₄ (no picture).

monoclinic VPO₄·H₂O [22]

Symmetric V–O–V chains, undistorted octahedra.

δ structure family

δ-VOPO₄ [6]

Unit cell viewed along a (top) and c axis (bottom).

ω-VOPO₄ [23]

Quadruple (2×2×1) unit cell viewed along a (top) and c axis (bottom).

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