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Original Oxocentered frameworks in $\text{Bi}_3(\text{VO}_4)\text{O}_3$ and $\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$ by Supercritical Steam.

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ABSTRACT: Two new bismuth oxo-vanadate $\text{Bi}_3(\text{VO}_4)\text{O}_3$ and oxo-arsenate $\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$ were prepared using supercritical hydrothermal pressure. Dealing with the anionic sublattice, both crystal structures are built on *anti* oxo- $\text{OBi}_4/\text{OBi}_3$, or $\text{OBi}_4/\text{OBi}_5$ units connected together in infinite corrugated 2D layers surrounded by isolated XO_4 ($\text{X} = \text{V}$ or As) tetrahedra. These edifices complete a series initiated by the recent $\text{Bi}_3(\text{PO}_4)\text{O}_3$ prepared in similar conditions. The latter being assigned to the “*simplest*” Bi-oxophosphate in terms of structural complexity, this aspect was investigated among the other compounds in their chemical ternaries. These phases are suggested to be high-pressure polymorphs not possible to tackle working at ambient pressure and temperature conditions.

A plethora of inorganic crystal structures have been described using the antiphase approach in which, unlike the standard model, the crystallographic units used for description are centered on the anions.¹ While anti-perovskites are clearly best suited for such structural descriptions, fluorites such as the 3D $\delta\text{-Bi}_2\text{O}_3$, clearly show the interest to analyze the oxo-centered frameworks, in several low dimensionality Bi-based compounds. It leads to the emergence of motifs made of oxo-centered $\text{O}(\text{Bi},\text{M})_x$ groups, best adapted for mega-series descriptions.^{2, 3, 4} In the last decades, many related structures based on OBi_4 building units were isolated and fully characterized. The anion-centered topologies also allow to predict new architectures of original oxo-centered based frameworks, surrounded by isolated spacers such as phosphates, vanadates, arsenates, molybdates, tungstates, or sulfates...^{5-11, 12} Recently, $\text{Bi}_3(\text{PO}_4)\text{O}_3$ ¹³ announced as “*the simplest bismuth(III) oxophosphate ever synthesized*” was prepared under supercritical hydrothermal pressure, around 50 MPa at 700K. Being aware of the size effects of PO_4 for AsO_4 or VO_4 substitution, the replacement of phosphate by bigger tetrahedral groups may give rise to innovative architectures and properties. For example, in $\text{BiCu}_2\text{O}_2(\text{PO}_4)$ and $\text{BiCu}_2\text{O}_2(\text{AsO}_4)$,¹³ different arrangements between same polycationic units exist and pressure-induced transformations from one form to another one,¹⁵ with important outcome concerning the associated low-D magnetism. In $\text{Bi}_6\text{ZnO}_7(\text{XO}_4)_2$ ($\text{X} = \text{P}, \text{As}$),¹⁶ the modification induced by P/As substitution breaks the spatial inversion (centrosymmetric/CS- PO_4 : CS vs. NCS- AsO_4) which is of great interest for nonlinear optical applications. Combining the HP-water method used by Aksenov *et al.*¹³ and chemical substitution is the leitmotif of this work. Supercritical water pressure conditions in autoclave yields two new crystal structures, isolated and structurally studied: **(1)** $\text{Bi}_3(\text{VO}_4)\text{O}_3$ and **(2)** $\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$. Their topologies are analyzed and compared to their oxo-phosphate variant $\text{Bi}_3(\text{PO}_4)\text{O}_3$ ranking their structural complexity.

Single crystals of **(1)** and **(2)** were obtained from the starting materials $(\text{BiO})_2\text{CO}_3$, NaVO_3 , K_2CO_3 (ratio 3:1:1) and $(\text{BiO})_2\text{CO}_3$, KH_2AsO_4 (ratio 3:1) respectively. In both cases, the potassium act as a mineralizer.¹⁷ 1 mg of the reactants mixture was sealed in a gold capsule half-filled of water, and placed during 3 days under counter supercritical water pressure in a Novaswiss autoclave, working at 450°C -150 bars for **(1)** and 700°C - 200 bars for **(2)**. At the end, the furnace was cut off and the autoclave left open at room temperature (RT) after cooling. The products were extracted from the tubes and washed several times with distilled water, filtered and finally dried at RT. Both samples contain colorless polycrystalline material and needle-shaped single crystals corresponding to the novel vanadate **(1)** (Figure S1) and arsenate **(2)** (Figure S2) respectively. The sample containing vanadium is inhomogeneous whereas the one containing arsenic is pure (Figure S3).

Crystal structures of **(1)** and **(2)** were refined by the single crystal X-ray diffraction method. The experimental data collection and refinement results are listed in tables S1 (for **(1)**) and S2 (for **(2)**). Crystal structure of **(1)** was refined in $P\bar{1}$ space group with unit cell parameters $a = 5.682(1)$ Å, $b = 8.479(2)$ Å, $c = 14.243(3)$ Å, $\alpha = 81.39(1)^\circ$, $\beta = 86.91(1)^\circ$ and $\gamma = 88.53(1)^\circ$ ($R_{\text{obs}} = 0.045$, $R_{\text{all}} = 0.051$, $\text{GOF} = 2.38$). **(2)** was refined in $P2_1/n$ space group with unit-cell parameters $a = 11.7264(14)$ Å, $b = 5.4063(7)$ Å, $c = 24.213(3)$ Å, $\beta = 98.66(1)^\circ$ ($R_{\text{obs}} = 0.039$, $R_{\text{all}} = 0.088$, $\text{GOF} = 1.09$).

These two new compounds are pertinent examples of well-adapted antiphase description.¹ Here, OBi_4 tetrahedra are associated to OBi_3 triangles and/or OBi_5 units leading to polycationic bidimensional (2D) oxo-centered units.

In the vanadate **(1)**, six independent oxygen are involved in OBi_4 tetrahedra (Td): O1, O2, O3, O5, O6 and O9. As in the homologous systems, the OBi_4 tetrahedra are strongly distorted with Bi-O distances varying from 2.128(11) Å for Bi1-O1 to 2.733(11) Å for Bi5-O6. They share edges to build a 4- Td -wide ribbon, decorated on both sides by OBi_5 square pyramids (SP) centered on O5, sharing their square-face with the ribbons. These polycationic ribbons are connected together through two edges connecting OBi_3 triangles (Tr) centered on O3, forming all together $[\text{Bi}_3\text{O}_3]^{3+}$ corrugated layers parallel to (010). For a better understanding, the layer is shown along different orientations figure S4. These layers sandwiched slabs of isolated VO_4 tetrahedra (figure 1a)), according to the refined formula of **(1)**: $\text{Bi}_3(\text{VO}_4)\text{O}_3$. An EDX study confirmed the presence of Bi and V in ratio 2.92/0.98 (figure S5). It involves very complex oxo-centered layers compared to the $[\text{BiO}]^+$ fluorite ones. Due to the steric effect of VO_4 groups, this new phase is different from the referenced $\text{Bi}_3(\text{PO}_4)\text{O}_3$ (figure 1b). In the latest, the structure shows also corrugated layers but built on double- Td -wide ribbons connected through association of two OBi_3 Tr . All crystallographic information are gathered tables 3-6.

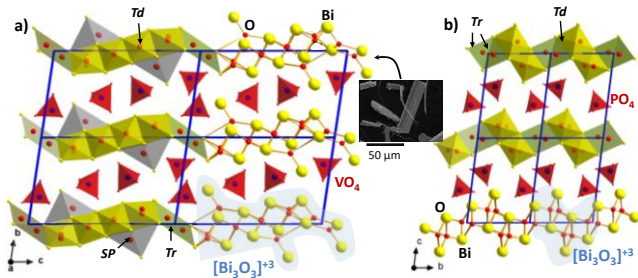


Figure 1: Projection of a) $\text{Bi}_3(\text{VO}_4)\text{O}_3$ and b) $\text{Bi}_3(\text{PO}_4)\text{O}_3$ along a axis. The anion-centered units are drawn in yellow for OBi_4 (Td), green for OBi_3 (Tr) and grey for OBi_5 (SP). XO_4 tetrahedra ($X= P$ and V) are shown in red. The inset shows the crystal shape of **(1)**.

The arsenate compound **(2)** displays the same kind of quadruple ribbons as found in **(1)**, built on the edge sharing of four OBi_4 Td centered on O1, O4, O8 and O10. There are also additional OBi_5 SP units (centered on O3) decorating the ribbons in their middle. The main difference with **(1)** lies in the layers (presented along different directions figure S6) where the ribbons are connected through triangles OBi_3 Tr (centered on O5, O15 and O16) by corner instead of edge as in **(1)**. Their associations form four member rings units hosting a local Bi-disorder (i.e. half-occupied Bi6a/Bi6b and Bi7a/Bi7b pairs, figure 2a and b) forming in-layer channels along b direction. However, on the Fourier map some residual electronic density still present close to the O15 atom suggesting the presence of hydroxyl groups pointing to the vacant space of the channels. The bond valence sum calculations (table S9) validate the assignment of the hydroxyl groups hold by O15, H1 and H2 atoms, and their presence is confirmed by infra-red spectroscopy (figure 2c). The wide and intense peaks observed in the $300\text{-}900\text{ cm}^{-1}$ region can be attributed to: a) the stretching vibration modes of arsenate groups AsO_4 , see $\text{PbCu}(\text{Fe}^{3+}, \text{Cu})(\text{AsO}_4)_2(\text{OH}, \text{H}_2\text{O})_2$ ²², and b) to Bi-O-Bi vibrations, see $\delta\text{-Bi}_2\text{O}_3$ (figure 2c).²³ The broad weak bands around 1300 cm^{-1} are attributed to O-H vibration in Bi-OH units, $\text{Bi}(\text{OH})_3$.²⁴ The broadness of this latter can plausibly be due to the hydroxides local disorders. Indeed, two 50% occupied OH bonds exist on O15. This disorder is linked to the local disorder on Bi6 and Bi7 mentioned above and allows local ordering such as sketched on figure 2. It significantly modifies Bi-O distances i.e. $\text{Bi7a/b-O16} = 2.395(14)/2.045(13)\text{ \AA}$ and $\text{Bi6a/b-O15} = 2.091(12)/2.236(12)\text{ \AA}$ depending on the proton presence or not. Finally, as in **(1)** the structure can be described by corrugated layers sandwiching isolated AsO_4 tetrahedra, showing similarities with structures detailed in ref 25. An EDX study confirmed the presence of Bi and As in expected ratio (figure S7). After structural refinement, the final formula is $\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$ and the corresponding crystal structure shown figure 2a). All main crystallographic information are detailed in tables S7-10.

To date, it was not possible to synthesize the Bi_3VO_7 phase at ambient pressure using solid-state synthesis from mixtures of Bi_2O_3 , V_2O_5 . The samples were systematically composed of known phases (BiVO_4 ,²⁶ $\text{Bi}_8\text{V}_2\text{O}_{17}$ ²⁷ and $\text{Bi}_{3.5}\text{V}_{1.2}\text{O}_{8.25}$ ²⁸) (figure S8). Also using solid state synthesis with Bi_2O_3 , $\text{Bi}(\text{OH})_3$ and As_2O_5 did not allow to obtain $\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$. It gave mixture of only known phases ($\alpha\text{-Bi}_2\text{O}_3$,²⁹ $\text{Bi}_{12}\text{As}_2\text{O}_{23}$,³⁰ and $\text{Bi}_{12.38}\text{As}_{0.62}\text{O}_{20.12}$ ³¹) (figure S9). Up to now, we tackled these two new phases by using only the supercritical water route. In addition, only **(2)** was prepared as a single material under conditions given above. (figure S3) As it is usually the case for such synthesis, the mineralizer and at the end of the reaction, is evacuated in the filtrate.

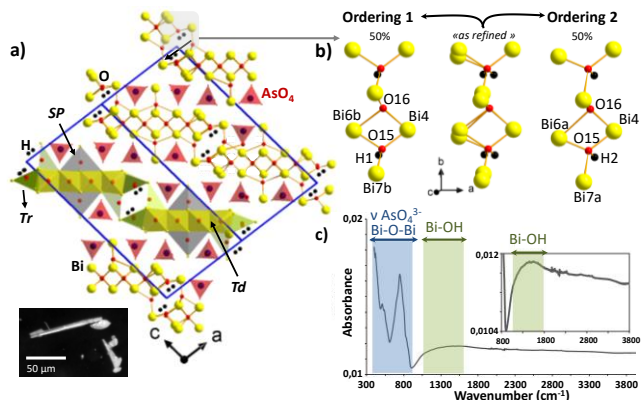


Figure 2: a) General overview of the new $\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$ along the b axis. The anion-centered units are drawn in yellow for OBi_4 (Td), green for OBi_3 (Tr) and grey for OBi_5 (SP) whereas AsO_4 groups are shown in red. The inset shows the crystal shape of **(2)**. b) Possible ordering between two consecutive ribbons, c) Infra-Red spectrum of crushed crystals of $\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$. The right inset shows the weak bands due to Bi-OH vibration.

$\text{Bi}_3(\text{PO}_4)\text{O}_3$ was analyzed on the basis of its structural complexity¹³ using Shannon information content per unit cell ($I_{G,\text{total}}$).³² In this prior work, it was described laconically as the simplest term in the oxo (hydroxo)-phosphate series. Indeed $I_{G,\text{total}}$ value varies from 76.104 to 2592.966 bits/unit cell for $\text{Bi}_3(\text{PO}_4)\text{O}_3$, with 2D corrugated layers, to $\text{Bi}_{14}\text{O}_{15}(\text{PO}_4)_4$ with 2D-thick blocks respectively. It denotes a versatile crystal-chemistry of oxo-centered polyhedra while associated with small phosphate groups ($r_{\text{P}5+}=0.17\text{ \AA}$). One could also plausibly suggest the effect of steam pressure for $\text{Bi}_3(\text{PO}_4)\text{O}_3$ leading to a more symmetrical edifice. A similar analysis on series of oxo (hydroxo)- vanadates and arsenates concerned here is summarized table 1.

The structural complexity per unit cell ($I_{G,\text{total}}$) were also calculated for **(1)** and **(2)** using details of calculation summarized in¹³ and³². The structural information amounts of **(1)** and **(2)** are respectively equal to 196.22 and 488.85 bits/unit cell.

The comparison with other vanadate and arsenate phases clearly reveals for bigger XO_4 groups ($r_{\text{As}5+/\text{V}5+} = 0.33\text{-}0.35\text{ \AA}$), a more homogeneous distribution of complexities ($I_{G,\text{total}}$ varying from 24.054 to 1016.355 bits unit cell for vanadates and from 64.426 to 488.85 bits/unit cell for arsenates). One must note that the bigger XO_4 groups drive less complex edifices, which pictures well a less labile matching between the XO_4 groups and the BiO_x oxo-centered framework. The most complex phase is a vanadate: $\text{Bi}_{14}\text{V}_4\text{O}_{30}$ (1016.35 bits/unit cell).³³ In comparison, the number of phases referenced in the literature for oxo (hydroxo)- arsenates is very limited: only three to date and two of them hosting hydroxides.

Clearly **(2)** is the most complex (hydro)oxo-arsenate of bismuth, it is mainly due to the structural disorder and $I_{G,\text{total}}$ drops to 513.53 bits/unit cell considering local ordering only. **(1)** stands in the lowest range in terms of complexities within its chemical series. Dealing within absence of O/OH tandem, similarly to the $\text{Bi}_3(\text{PO}_4)\text{O}_3$ case, the high-pressure conditions may be responsible for its relatively simple (i.e. symmetrical) structure. It is of course far below the complexity calculated for some Bi-based minerals such as the Bouazzerite $\text{Bi}_6(\text{Mg}, \text{Co})_{11}\text{Fe}_{14}(\text{AsO}_4)_{18}\text{O}_{12}(\text{OH})_4(\text{H}_2\text{O})_{86}$ ³⁴ ($I_{G,\text{total}} = 3035.201$ bits/cell) in which natural conditions brewed a diversity of cationic species. Taking into account that our experimental conditions using super-critical water steam vapor may simulate some mineralogical conditions, it emphasizes the broad perspectives offered by working in more rich and more diversified chemical systems.

Conclusion. Considering the title compounds and the phosphate equivalent of (1), $\text{Bi}_3(\text{PO}_4)_3\text{O}_3$, the XO_4 size effect drastically impact the crystal structure substituting P^{5+} by V^{5+} or As^{5+} . We observed a true preference of the oxo-centered framework for fluorite-type 2D slabs separated by XO_4 entities, which topology and complexity are versatile.¹⁶ In these rich chemical systems, the supercritical water-pressure parameter is barely used now, while it is

shown here to open wide prospective possibilities. It seems very promising to further stabilize stable or metastable compounds into more complex Bi-based chemical systems. Especially, the possibility to isolate new bismuth vanadate is promising considering the broad impact of BiVO_4 in the current development of new catalytic, luminescent and photocatalytic materials.⁴⁵⁻⁴⁶

TABLE 1. Complexity of each Bi/V/O +H and Bi/As/O +H members of existing phases Containing Oxo-Centered Tetrahedrons.

Compound/Mineral	S.G. Z	a (Å), α (°)	b (Å), β (°)	c (Å), γ (°)	V [Å ³]	v (atoms)	IG, total (bits/u.c.)	Synthesis route
$\text{Bi}_4(\text{VO}_{3.5})_2\text{O}_4^{35}$	C2/m 6	5.6120(2)	15.2829(4) 89.756(1)	16.60139(50)	1423.85	11	24.054	Solid state synth at 850°C
$\text{Bi}_6(\text{VO}_{3.33})_3\text{O}_6^{36}$	Pnma 4	5.4721(1)	17.2542(3)	14.9174(2)	1408.45	100	384.386	Sealed tube under vacuum at 650°C
$\text{Bi}_4(\text{VO}_{3.5})_2\text{O}_4^{37}$	I4/mmm 1	3.99172(5)	3.99172(5)	15.4309(3)	245.87	11	24.054	Solid state synth at 800°C
$\text{Bi}_4(\text{VO}_{3.5})_2\text{O}_4^{37}$	Amam 4	11.2331(3)	5.6491(2)	15.3469(3)	973.87	36	102.117	Solid state synth at 800°C + slow cooling at 300°C.
$\text{Bi}_6(\text{VO}_4)_8\text{O}_7^{38}$	C2/m 2	20.02938(5)	11.59621(3) 111.3366(2)	21.12860(6)	4571.07	150	834.323	Solid state synth at 825°C
$\text{Bi}_{14}(\text{VO}_4)_4\text{O}_{14}^{39}$	C2/c 8	9.9345(3)	11.5464(2) 110.8813(9)	27.9515(4)	6011.09	184	1016.355	Solid state synth at 800°C
$\text{Bi}_{23}(\text{VO}_4)_4\text{O}_{28}^{40}$	Immm 1	12.1371(4)	11.6935(4)	16.0191(6)	2273.51	84	342.955	Solid state synth at 800°C
$\text{Bi}_2(\text{VO}_4)\text{O}(\text{OH})^{41}$	P2 ₁ /c 4	6.971(1)	7.535(1)	10.881(1)	546.57	36	114.117	Mineral
$\text{Bi}_3(\text{VO}_4)_3$ [this work]	P-1 2	5.6823(12) 81.39(1)	8.4789(19) 86.91(1)	14.2428(26) 88.5287(1)	677.39	44	196.22	This work
$\text{Bi}_2(\text{AsO}_4)_{1.7}\text{O}_{33.2}^{42}$	I23 1	10.2094(5)	10.2094	10.2094	1064.14	33	64.426	Precipitation
$\text{Bi}_3(\text{AsO}_4)_2(\text{OH})\text{O}^{43}$	P-1 2	9.993(3) 87.82(2)	7.404(3) 115.01(2)	6.937(3) 111.07(2)	430.07	30	117.207	Mineral
$\text{Bi}_2(\text{AsO}_4)(\text{OH})\text{O}^{44}$	P2 ₁ /c 4	7.000(2)	107.08(2)	10.831(2)	538.48	36	114.117	Mineral
$\text{Bi}_{3.5}(\text{AsO}_4)(\text{OH})_{0.5}\text{O}_{3.5}$ [this work]	P2 ₁ /n	11.7264(14)	5.4063(7) 98.66(1)	24.2131(30)	1517.51	104	488.85	This work

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XX.XXXX/acs.inorgchem.xxxxx. SEM images, EDS analysis, powder XRD data, and results of crystal structure refinements.

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Author Contributions

The manuscript was written through contributions of all authors and all of them have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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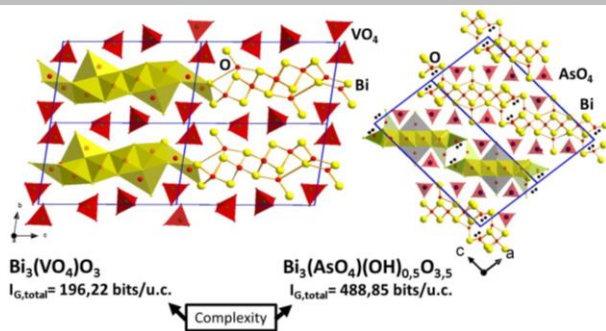
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Table of Content



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**Original Oxocentered frameworks in
Bi₃(VO₄)O₃ and Bi_{3.5}(AsO₄)(OH)_{0.5}O_{3.5}
by Supercritical Steam.**

Two new bismuth oxo-vanadate Bi₃(VO₄)O₃ and oxo-arsenate Bi_{3.5}(AsO₄)(OH)_{0.5}O_{3.5} were prepared using supercritical hydrothermal pressure. Their crystal structure and complexity are compared together and with the previously reported phosphate analogue Bi₃(PO₄)O₃.