

Sol gel-based synthesis of the phosphorus-containing MAX Phase V₂PC

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ABSTRACT: More than 150 MAX phases are known to date. Their chemical diversity is the result of mixing-and-matching early-to-mid transition metals (*M*), main group elements (*A*) and carbon and/or nitrogen (*X*). The vast majority of the respective carbides and (carbo)nitrides contain group 13 and 14 as the *A* element, such as Al, Ga, and Si. V₂PC is amongst the least studied members of this family of materials, as a matter of fact, it is only mentioned in two pieces of original literature. The solid-state synthesis is extremely vaguely described and working with elemental phosphorus poses additional synthetic challenges. Here, we confirm these experimental difficulties and present an alternative sol gel-based approach to prepare almost single-phase V₂PC. The versatility of the sol gel chemistry is further demonstrated by variation of the gel-building agent moving beyond citric acid as the carbon source. DFT calculations support the experimentally obtained structural parameters and show V₂PC is a metal.

The field of transition metal phosphides, borides, and carbides encompasses a large and vibrant chemical range.^{1,2,3,4} Similarly, the potential applications are broad, ranging from the huge field of energy storage and conversion¹ to magnetic storage⁵, refrigeration, and directed drug delivery⁶ on the phosphide side. Carbides, in addition, are discussed in areas requiring more ceramic-like properties, such as hardness and refractoriness in, for example, industrial tools.⁷ The family of MAX phases (M_{n+1}AX_n),⁸ have attracted considerable interest in the areas mentioned above. Comprising both early-to-mid transition metals (*M*), and mostly main group metals (*A*), these carbides (or (carbo)nitrides; *X* = C and/or N) offer great chemical and compositional variety. Discovered in 1960 for the sulfur containing Zr-carbides,⁹ and quickly thereafter coined as H-phases by Nowotny and coworkers^{10–14} during the 1960s and 70s, this class is today heavily researched ever since the works by Barsoum *et al.* in the 1990s.¹⁵

Although there are about 150 known members today,¹⁶ many of them have only ever been described by Nowotny's group decades ago. Today's research focus lies on the Ti-Al systems, in parts because of the discovery of two-dimensional MXenes about 10 years ago.¹⁷ Nevertheless, the compositional range of MAX phases is not exhausted or even fully taken advantage of, especially the more exotic members, including P or S containing phases. None of these exotic species are being studied and the literature only knows

the original and first publication on their existence. Exhausting said chemical range might entail intriguing findings, as MAX phases offer an interesting mix of properties as it is. MAX phases conventionally combine both metallic and ceramic properties. Outside the realm of electrical and thermal conduction, oxidation resistance, stiffness, and refractoriness are also exhibited, to name a few.⁸

Besides the MXene focus of the community, synthetic hurdles come to mind, potentially because the non-metallic *A* group metals P, S, or As are not as commonly used or considered. The lack of literature, however, clearly demands the community's attention. The original work on V₂PC,¹⁸ for instance, very vaguely describes the solid-state synthesis of this MAX phase in a *very* short communication. Synthetic details, besides "the usual manner of annealing powder mixtures at 1000°C", are not elaborated on (and assume fluency in German). After intense investigation of the literature, another publication on this phase was found that elaborates on the complexity of the phase diagram of V-P-C.¹⁹ On top of that, working with elemental phosphorous comes with its own intricacies, namely the low melting and boiling points, as well as the hazards of creating flammable and toxic white phosphorus.²⁰

Considering all these obstacles, it is not surprising that V_2PC is effectively not being studied. In order to circumvent some of these hurdles, sol gel chemistry is a viable synthetic alternative. It was shown in a series of recent publications, that MAX phases can be accessed via sol gel syntheses,^{21,22} and additionally, the morphology can be controlled.^{23,24} Starting from molecular, and non-elemental precursors, mass diffusion pathways are drastically shortened, allowing for shorter reaction times as well as lower reaction temperatures.²⁵ The gel-forming agent is interchangeable and allows for a variety of choices, depending on the synthetic goal.²⁵

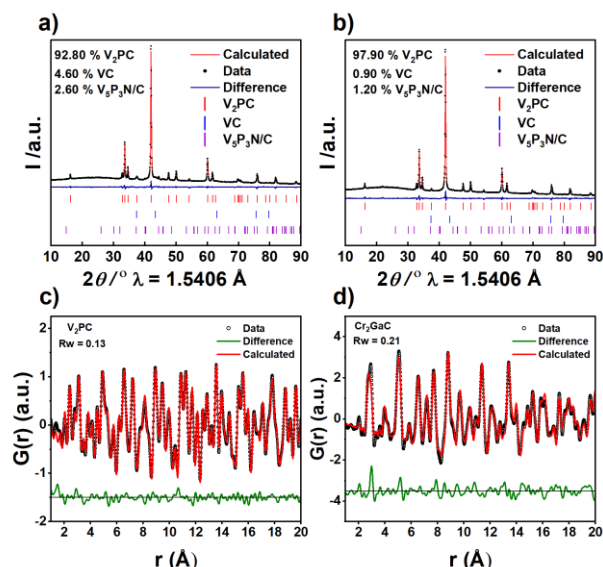
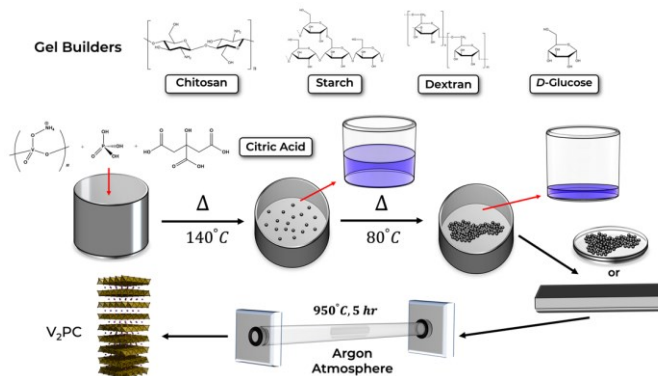


Figure 1: (a) As-prepared V_2PC prepared with citric acid as the C source (b) Acid-washed citric acid based V_2PC sample (13 d). Comparison of refined PDF data of (c) V_2PC prepared at 950 °C and (d) Cr_2GaC prepared at 1050 °C.¹⁹

Our sol gel-based approach trivializes the synthesis of V_2PC comparatively to solid-state methods where yields were nonexistent (in our group). Briefly, for the sol gel-based strategy, water soluble metal salts (e.g. of V as the M element) as well as phosphoric acid (A element source) and a carbon-containing gel building agent are mixed, dried and heated to form the target MAX phase V_2PC (see SI). A typical solid-state synthesis involves the reaction of elemental vanadium, graphite, and red phosphorus at high temperatures. As it stands, there is a large uncertainty in what specific temperature regimes V_2PC is stable at. Nowotny's original work¹⁸ on this compound provides rather vague insight with a reaction profile reaching a maximum temperature of 1000 °C. A detailed discussion of all attempts of obtaining V_2PC via solid-state methods is expanded upon in the Supporting Information (Tables S2, S3, Figures S5-S8). With no success in obtaining the V_2PC MAX phase, the search for other viable methods namely sol gel chemistry became very crucial. This is even more apparent when looking into the phase diagram of the ternary V-P-C system. It is found that V_2PC exists with a rather miniscule phase homogeneity range.¹⁹ Due to this, phases such as the non-stoichiometric $V_5P_{2.83}C_{0.5}$, binary VC, and even graphitic species

Scheme 1. A schematic of the experimental methodology that is used when making the V_2PC MAX phase by means of sol-gel synthesis.



have a larger chance to crystallize preferably over V_2PC . Sol gel-based syntheses fortunately offer more synthetic parameters to be varied in contrast to solid-state methods, typically only varying the V-P-C stoichiometry and temperature profiles. The X-ray powder diffraction data of the as-prepared as well as acid washed products prepared with citric acid are shown in Figure 1 (a) and (b). In both cases, the MAX phase is the main phase while VC and V_5P_3N/C are identified as minor side phases that can almost completely be removed by the acid wash (compare (a) and (b)).

V_5P_3N/C formation becomes possible because ammonium metavanadate (NH_4VO_3) is used as a vanadium source. As a result of this, it cannot be completely ruled out that nitrogen-containing side phases have the potential to crystallize. Looking more into this, the original publication on the synthesis of V_2PC ¹⁸ also briefly outlines the stoichiometric phase V_5P_3N . Analyzing the characteristic Powder X-Ray diffraction peaks of this phase, the Miller Indices of (211), (300), and (112) correspond to 2θ angles of 44.5, 45.6, and 46.3. Comparatively with the non-stoichiometric phase $V_5P_{2.83}C_{0.5}$, 2θ angles of 44.0, 45.2, and 45.8 are observed which are almost identical to the stoichiometric V_5P_3N . Distinguishing between the two phases would be extremely complex. To avoid any further convolution, it was imperative that both these phases in some capacity be incorporated into the Rietveld refinements of the as-synthesized and acid-washed samples. Hence why the particular phase in Figure 1 (a) is intentionally written as V_5P_3N/C .

The local structure of the understudied V_2PC was compared with that of Cr_2GaC , which was also synthesized via sol gel-based synthesis by our group¹⁹ (Figure 1 (c) and (d)). Remaining low r peaks confirm the expected atom-atom distances for the MAX phase structure: For Cr_2GaC (Figure 1(d)), 2.0 Å, 2.5 Å, and 2.8 Å correspond to Cr-C, Cr-Ga (2.65 Å), and Cr-Cr, respectively. For V_2PC (Figure 1 (c)), 2.0 Å, 2.4 Å, and 2.8 Å correspond to V-C, V-P, and V-V, respectively. The crystalline model used in the Rietveld refinement provides a good description of the entire PDF and is therefore a good description of the local and average structure of the synthesized V_2PC . This shows that there is no local disordering in the formed material and that the reaction temperature of 950 °C is optimal for sample crystallinity.

Table 1. Composition of as-prepared samples using different C sources obtained by Rietveld refinements of the XRD data.

Carbon Source (w.t.%)	V ₂ PC	VC	V ₅ P _{2.83} C _{0.5}	C
Citric Acid	90.1	4.3	5.6	--
Dextran	83.4	12.8	3.75	--
Starch	62.6	16.3	18.9	2.1
D-Glucose	64.0	8.0	10.2	17.0
Chitosan	37.8	47.0	6.9	8.0

Table 2. Composition of the acid-washed samples prepared with different C sources obtained by Rietveld refinements of the XRD data.

Carbon Source (w.t.%)	V ₂ PC	VC	V ₅ P _{2.83} C _{0.5}	C
Citric Acid	93.5	2.6	3.9	--
Dextran	84.5	11.0	4.5	--
Starch	76.8	11.7	10.2	1.4
D-Glucose	66.0	7.0	6.5	21.0
Chitosan	38.0	45.0	3.2	14.0

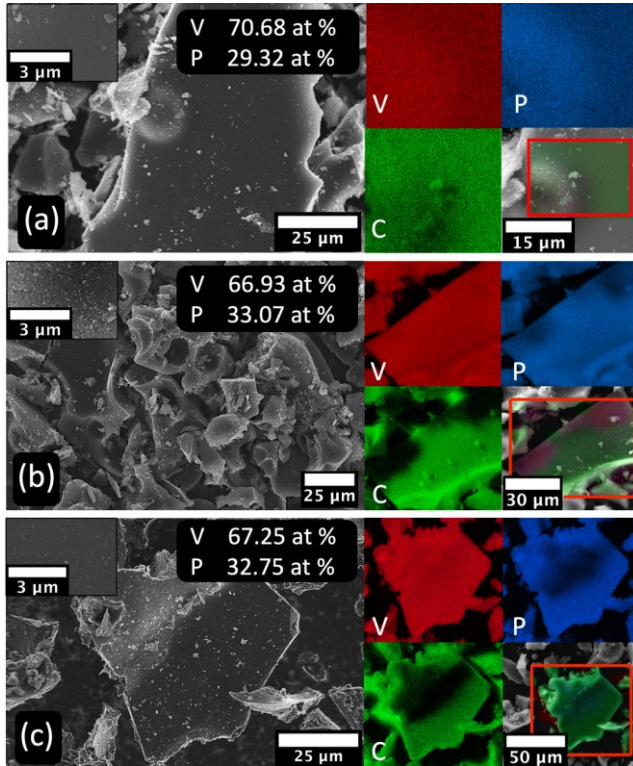


Figure 2. SEM imaging and EDS analysis of (a) As-prepared V₂PC with citric acid as the C source, (b) Acid-washed sample after 24 hours (H₂SO₄) (c) Acid-washed sample prolonged H₂SO₄ exposure (13 days).

The beauty of these sol gel-based syntheses is that the ingredients can readily be varied. All chosen gel-builders/C sources (citric acid, dextran, starch, d-glucose, chitosan) lead to the formation of the target compound V₂PC, however, with some differences in yields. The effect of the carbon source on the product composition as determined by analysis of the X-ray powder diffraction data (see Figure S10-12, in Supporting information) and is summarized in Table 1. The citric acid-based sol-gel synthesis of V₂PC readily produces 90+ % MAX phase utilizing optimized synthesis parameters (as-prepared samples). Alternative gel

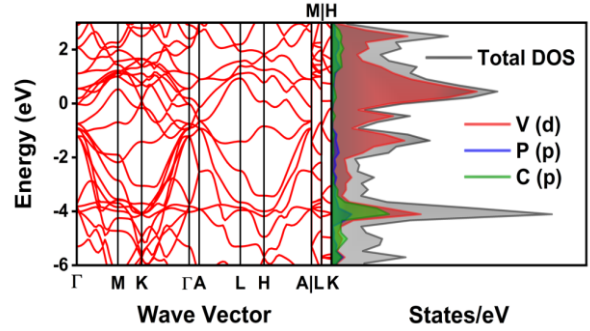


Figure 3. A depiction of the band structure and Projected Density of States of the V₂PC MAX phase generated from theoretically calculated lattice parameters.

builder yields are outlined again in Table 1. Washing the samples, independent of the used C source, leads to removal of side phases with an increase in MAX phase yield (Table 2). The crystallinity of the products after acid washings is not diminished when exposed for longer periods of time. Figure 2 shows the microstructure and composition of an as-synthesized sample prepared with citric acid, a 24-hour acid-washed sample, and an acid-washed sample after prolonged exposure, respectively. Drawing comparisons between the samples, the as-synthesized sample (Figure 2 (a)) exhibits a very smooth surface. The 24h-washed sample (Figure 2 (b)) shows signs of the etching process with craters and more rugged surfaces which is the result of the removal of side phases. Figure 2 (c) shows the sample's surface after prolonged acid exposure (13 days).

The morphologies when utilizing other C sources do not differ immensely from the structures obtained with citric acid (see Figure S15).

Table 3. Lattice Parameter Comparison of the V₂PC MAX phase.

Lattice Parameters	Experimental	Literature ²⁶	Computed
a	3.078	3.074	3.071
c	10.924	10.910	10.900

To gain insights into phase stability and electronic structure, the formation energy and band structure of V₂PC are further investigated by the DFT method. The optimized lattice constants agree well with the experimental values and

the data in the Materials Project, as listed in Table 3. Furthermore, the formation energy of this phase is observed as thermodynamically formable. The calculated value is -0.712 eV/atom, which matches the value of -0.687 eV/atom from the Materials Project well. Figure 3 shows the band structure of the V₂PC, displaying the phase is a metallic system, namely hole and electron bands crossing the Fermi level along the whole Brillouin zone. Further, the electronic states around the Fermi level are dominated by the 3d orbitals of V atoms, with a small contribution from the P and C p orbitals.

In summary, a facile sol gel-based synthesis of the highly understudied MAX phase V₂PC is presented. This approach based on water-soluble metal salts avoids the complications that arise from the classical solid-state synthesis based on elemental phosphorous. Moreover, we demonstrate the versatility of this synthesis technique by using not only citric acid as the gel-builder and carbon source, but a multitude of polymeric or monomeric carbohydrate species. V₂PC is obtained almost single-phase after removal of minor side phases through an acid wash, and the structural parameters obtained from X-ray powder diffraction are confirmed by theoretical calculations. The latter also predict V₂PC to be a metallic conductor making it fit in with all of the other MAX phase members. The sol gel-based approach therefore offers a springboard for the synthesis of various other “more exotic” MAX phases, especially those with “unconventional” A elements, that may otherwise be inaccessible via solid-state methods. Furthermore, it may pave the way to additional phosphorous-containing compounds, e.g. phosphides, which are hardly accessible or pose significant challenges by solid-state chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information. Additional experimental details, including the solid-state reactions, XRD data, and Rietveld refinements, SEM/EDS analysis, and PDF refinements.

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Author Contributions

J. Sinclair synthesized and analyzed the samples and wrote the manuscript. J. P. Siebert analyzed the samples and wrote the manuscript. M. J. performed the synchrotron XRD measurements and assisted in the total scattering analysis. S. Chen provided the computational analysis. C. S. Birkel provided the research question, wrote and reviewed the manuscript.

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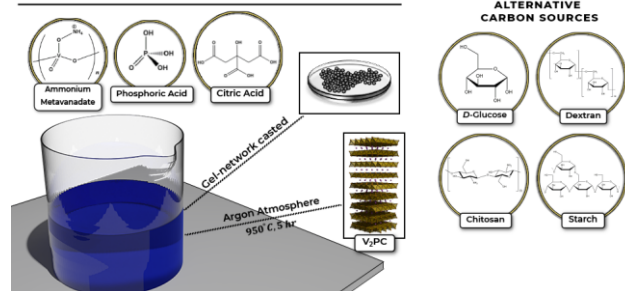
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SOL-GEL SYNTHESIS



We have developed a sol gel-based synthesis of the largely unknown MAX phase V_2PC and demonstrated the use of varying carbon sources. With an optimized synthesis protocol, including an acid wash, the product consists of $\sim 98\%$ V_2PC , small amounts of carbide/carbonitride side phases (crystalline) and amorphous carbon. This convenient method can open the path to further (hitherto unknown) phosphides.