



Non-noble metal vanadium phosphites with broad absorption for photocatalytic hydrogen evolution



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ABSTRACT

We reported the synthesis and crystal structures of alkali metal and alkali-earth metal phosphite, namely, CsV₂(H₃O)(HPO₃)₄ (**1**), and Ba₃V₂(HPO₃)₆ (**2**). Both compounds were prepared by hydrothermal reactions and feature unique new structures. They both exhibit 3D complicated frameworks based on VO₆ octahedra which are connected by HPO₃ tetrahedra via corner-sharing. Alkali or alkali earth metal cations are filled in the different channels of the frameworks. Topological analysis shows that the framework of CsV₂(H₃O)(HPO₃)₄ (**1**) is a new 3,3,3,4,5-connected network with the Schläfli symbol of {4.6²}₂{4².6⁶.8²}{6³}{6⁵.8}. The investigations of X-ray photoelectron spectroscopy (XPS) and magnetic measurement on CsV₂(H₃O)(HPO₃)₄ suggest a +3 oxidation state of the vanadium ions in compound **1**. Photocatalytic performance was evaluated by photocatalytic H₂ evolution and degradation of methylene blue, which shows that both compounds exhibit activity under visible-light irradiation. IR spectrum, UV–vis-NIR spectrum and thermogravimetric analysis (TGA) of compounds were also investigated.

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1. Introduction

As an attractive and vast class of inorganic materials, metal phosphites have attracted more and more attentions due to their unique crystal structures and tremendous potential applications in various areas, such as catalysis, photochemistry, gas sorption, magnetism and nonlinear optics [1–6]. Different from the widely reported 4-connected PO₄ tetrahedra, HPO₃ anion offers three P–O bonds and one P–H bond lead into a unique pseudo tetrahedron unit. This special pseudo tetrahedron unit may facilitate the discovery of zeolite-type materials by interrupting partly covalent bond connections of framework structures. As a result, extra-large channels are more likely to appear in this situation. For example, Lin et al. reported a multi-porous gallium zincophosphite recently, which contains different 48-membered ring (48 MR), 56 MR, 64 MR, and 72 MR [5–9]. To date, by using organic molecules as structure-directing templates, a large amount of metal phosphites open frameworks have been synthesized under the hydrothermal conditions [4–10]. However, the presence of organic molecules inside the structures would largely reduce their thermal stability and applicability. Compared with this kind of organic–inorganic

hybrid metal phosphites, pure inorganic metal phosphites greatly improve their thermal stability and have already been exploited in various fields [1–2]. For inorganic metal phosphites, in cathode material area, Li₃Fe₂(HPO₃)₃Cl [11] and Li_{1.43}[Fe_{4.43}^{II}Fe_{0.57}^{III}(HPO₃)₆] · 1.5H₂O [12] show a reversible capacity of 70 mA h g^{−1} and 12 mA h g^{−1}, respectively. In magnetic material area, a series of transition-metal (TM) phosphites, such as Na₂M(HPO₃)₂ (M = Ni, Fe, Co) and A [M(HPO₃)₂] (A = K, NH₄, Rb and M = V, Fe) have been reported and feature different magnetic properties [13–16]. In frequency transfer material area, two main-group metal phosphites, namely, SnHPO₃ [17] and RbIn(HPO₃)₂ [18], exhibit second harmonic generation (SHG) responses. All these above-mentioned compounds display different properties with interesting structures. Thus, pursuing for new metal phosphites with fascinating crystal structures and interesting physical are not allowed for any delay.

As semiconductor materials, metal orthophosphates have been proved to be a type of high efficient photocatalytic materials. For examples, Ag₃PO₄ [19a,b] showed a good photocatalytic performance under visible-light irradiation, and Cu₂(OH)PO₄ was reported as an strong near-infrared (NIR) activated photocatalyst [19c]. Although bandgap measurements of metal phosphites show that they also have strong absorption in NIR and visible range [6], however, the photocatalytic properties of metal phosphites haven't been reported yet. As claim above, by aiming at new metal phosphite semiconductor materials, we induce alkali metal or alkali-earth metal into vanadium-phosphite system to adjust their

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absorption edges in IR or NIR region which may affect their photocatalytic properties. In this article, two new metal vanadium phosphites, formulated as $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ (**1**) and $\text{Ba}_3\text{V}_2(\text{HPO}_3)_6$ (**2**), have been prepared under hydrothermal reaction. In this paper, we present the syntheses, crystal structures, optical properties and photocatalytic performance of our new compounds. This study may provide a new strategy for design of novel photocatalytic materials based on metal phosphites in the future.

2. Experimental section

2.1. Materials and methods.

Cs_2CO_3 , BaCO_3 , NaVO_3 and H_3PO_3 aqueous solution (50%) were purchased from Shanghai Reagent Factory (AR, 99.0%) and used without further purification. IR spectra were recorded on a Magna 750 Fourier transform infrared (FT-IR) spectrometer as KBr pellets in the range of $4000\text{--}450\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} at room temperature. Optical diffuse reflectance and UV spectra were measured at room temperature with a Perkin-Elmer Lambda 900 UV-vis-NIR spectrophotometer and a BaSO_4 plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectra using the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient (which is practically wavelength independent when the particle size is larger than $5\text{ }\mu\text{m}$), and R is the reflectance [20]. X-ray powder diffraction (XRD) patterns were collected on a Rigaku MiniFlex II diffractometer using $\text{Cu-K}\alpha$ radiation in the angular range of $2\theta = 5\text{--}80^\circ$ with a step size of 0.2° . Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses were performed on a NETZCH STA449C unit at a heating rate of $15\text{ }^\circ\text{C min}^{-1}$ under N_2 and air atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI Quantum 2000 XPS system with a monochromatic $\text{Al-K}\alpha$ source and a charge neutralizer. The C-1s peak at 284.8 eV of the surface adventitious carbon as a reference material to survey the binding energies of compounds. Magnetic susceptibilities were performed on a Quantum Design MPMS-XL SQUID magnetometer. X-ray diffraction data collection for $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ and $\text{Ba}_3\text{V}_2(\text{HPO}_3)_6$ were performed on a Rigaku Mercury CCD diffractometer with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 293 (2) K. The data sets were corrected for Lorentz and polarization factors as well as absorption by the multi-scan method [21]. The structure was solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters except for O(1) in $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$, which was refined with 'isor' instruction. If this constraint is not applied, the displacement parameters for O(1) will be abnormally small. All the H atoms in $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ and $\text{Ba}_3\text{V}_2(\text{HPO}_3)_6$ were needed and assigned to P-H bonds and O(9) in $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ is assigned to protonated water molecules on account of charge balance and bond valence calculations, but they were not refined due to the difficulty in the determination of their precise locations. The structure of compounds was also checked for possible missing symmetry with PLATON. Crystallographic data and structural refinements are summarized in Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters, important bond distances and angles are listed in Table S1 and S2, respectively. Further details of the crystal structure studies can be obtained from the FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (49) 7247808666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD 430149 for compound **1** and 430148 for compound **2**.

Table 1

Crystal data and structural refinements for $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ and $\text{Ba}_3\text{V}_2(\text{HPO}_3)_6$.

Compound	1	2
Empirical formula	$\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$	$\text{Ba}_3\text{V}_2(\text{HPO}_3)_6$
Formula weight	573.72	993.74
Crystal system	Orthorhombic	Trigonal
Space group	$Pbam$ (No. 55)	$R\bar{3}$ (No. 148)
Wavelength	0.71073 \AA	0.71073 \AA
$a/\text{\AA}$	14.7657(15)	15.712(4)
$b/\text{\AA}$	16.6558(16)	15.712(4)
$c/\text{\AA}$	5.2388(6)	12.911(7)
$V/\text{\AA}^3$	1288.4(2)	2760.3(18)
Z	4	6
$D_c/\text{g cm}^{-3}$	2.953	3.587
$\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$	4.795	7.912
$F(000)$	1084	2688
Completeness to $\theta = 27.46$	99.3%	99.8%
Goodness-of-fit on F^2	1.119	1.154
Final R indices [$I > 2\sigma$]	$R_1 = 0.0700$, $wR_2 = 0.1719$	$R_1 = 0.0374$, $wR_2 = 0.0906$
R indices (all data)	$R_1 = 0.0742$, $wR_2 = 0.1752$	$R_1 = 0.0494$, $wR_2 = 0.0961$
Largest diff. peak and hole	3.839 and -1.396 e \AA^{-3}	1.805 and -2.004 e \AA^{-3}

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \omega R_2 = \{ \sum w [(F_o)^2 - (F_c)^2]^2 / \sum w [(F_o)^2]^2 \}^{1/2}.$$

2.2. Photocatalytic performance

The photocatalytic performance of both compound **1** and **2** was evaluated by the photocatalytic H_2 evolution and the degradation of methylene blue (MB) in a 300 W Xe lamp equipped with a 420 nm cutoff filter to remove all wavelengths lower than 420 nm and provide the visible light irradiations. For photo-catalytic H_2 evolution experiments, reactions were carried out in a closed gas circulation and evacuation system fitted with a top Pyrex window. 50 mg of photocatalyst was dispersed in 100 mL of aqueous solution containing 0.5 M Na_2SO_3 and 0.43 M Na_2S as sacrificial reagents. The amount of H_2 evolved was determined with an on-line gas chromatography equipped with a TCD detector. For photodegradation experiments, 50 mg of photocatalyst was suspended in 40 mL of MB aqueous solution (10 ppm). Before irradiations, the suspension was magnetically stirred in the dark for several hours to ensure adsorption-desorption equilibrium. During the irradiation, at given irradiation time intervals, 3.0 mL suspension was taken out regularly and the supernatant was centrifuged and filtered to separate the photocatalyst. The filtrate was collected and analyzed by a UV-vis spectrophotometer. The absorption peak at 664 nm wavelength for MB was monitored in sequence to detect the MB concentrations in the solution after irradiation. During the photocatalytic reaction, the temperature of the reactant solution was controlled at room temperature by a flow of cooling water.

2.3. Synthesis

2.3.1. Synthesis of $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ (**1**)

A mixture of Cs_2CO_3 (10.0 mmol, 1.570 g), NaVO_3 (0.787 g, 0.65 mmol), H_3PO_3 (5.0 mL) and H_2O (10.0 mL) was sealed in an autoclave equipped with a Teflon liner (25 mL), heated at $210\text{ }^\circ\text{C}$ for 4 days and finally slowly cooled to room temperature at a rate of $5\text{ }^\circ\text{C/h}$. The initial and final pH value of the reaction media was about 0.5 and 1.0, respectively. For the acid reaction condition, the additional protons should be distributed the water molecular, and the hydroxonium ion formulation give a formulation of $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$. The product was washed with water and ethanol and then dried in air. Green prismatic crystals of $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ were collected with a yield of about 83% (based on NaVO_3). The EDS analysis of $\text{CsV}_2(\text{H}_3\text{O})(\text{HPO}_3)_4$ confirms the Cs/V/P/O

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