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# High-Pressure Metathesis of the $M_{1-x}PO_{3+4x}N_{1-4x}$ ( $x \approx 0.05$ ) and $M_{0.75}PO_4$ (M = Zr, Hf) Orthophosphates

Simon D. Kloß, Andreas Weis, Sophia Wandelt, and Wolfgang Schnick\*0

Department of Chemistry, University of Munich (LMU), Butenandtstraße 5-13, 81377 Munich, Germany

#### **S** Supporting Information

**ABSTRACT:** We describe the oxonitridophosphates  $M_{1-x}PO_{3+4x}N_{1-4x}$  ( $x \approx 0.05$ ) and the isotypic oxophosphates  $M_{0.75}PO_4$  (M = Zr, Hf) obtained by high-pressure metathesis. The structures ( $ZrSiO_4$ -type, space group  $I4_1/amd$  (no. 141), a = 6.5335(7) - 6.6178(12), c = 5.7699(7) - 5.8409(9) Å, Z = 4) were refined from single-crystal X-ray diffraction data, and the powder samples were examined with quantitative Rietveld refinement. Infrared spectroscopy did not indicate the presence of X-H (X = O, N) bonds. The optical band gaps, between 3.5 and 4.3 eV, were estimated from UV-vis data using the Kubelka–Munk function under assumption of a direct band gap. Temperature-dependent powder X-ray diffraction showed a phase transformation of the  $M_{0.75}PO_4$ 



(M = Zr, Hf) compounds to ambient pressure polymorphs at 780 (Zr) and 900 °C (Hf). The preparation of the nitrogen containing compounds exemplifies the systematic access to the new class of group 4 nitridophosphates granted by high-pressure metathesis. Moreover, we show that high-pressure metathesis can also be used for the preparation of metastable oxophosphates.

### INTRODUCTION

High-pressure metathesis using the multianvil technique was the first synthesis route to offer fast and efficient access to oxonitridophosphates with trivalent rare-earth metals and, moreover, providing the means to systematically direct the structures' anion networks.<sup>1-4</sup> Recently, high-pressure metathesis was successfully expanded to nitridophosphates with the group 4 metal Hf. As the first instance of this class of compounds the oxonitridophosphate  $Hf_{9-x}P_{24}N_{52-4x}O_{4x}$  (x  $\approx$ 1.84), which consists of two interpenetrating diamond-like anion frameworks, has been prepared.<sup>5</sup> While this compound has been a first proof of principle, one strong-point of highpressure metathesis for nitridophosphates, however, is the granted control over the formed anion network. For the rare earths, for example, the flexible anion networks range from highly condensed frameworks down to noncondensed tetrahedra.<sup>1–4</sup> This systematic tuning of the network type has yet to be proven for group 4 nitridophosphates.

The inherent challenge during synthesis of transition metal nitridophosphates is a competitive redox reaction by which the nitride ion is oxidized and transition metal phosphides are formed.<sup>5</sup> Previous synthesis routes to transition metal nitridophosphates led only to scarce success most likely due to unsuitable reaction conditions, e.g. lack of high-pressure methods, or unsuitable starting materials, e.g. lack of metal azides or reactive nitrides.<sup>6–9</sup> The existence of nitridosodalites, which were prepared at ambient pressures, showed stability of transition metals embedded in a nitridophosphate network.<sup>10,11</sup> No synthesis route, however, was discovered yet that grants

control over the formed anion network. High-pressure metathesis may remedy these problems. It starts from reaction of readily available metal halides with  $LiPN_2$  under pressures of several GPa (eq 1), a concept which is in principle transferable to almost all metals of the periodic system:<sup>1</sup>

$$MHal_{x} + xLiPN_{2} \rightarrow MP_{x}N_{2x} + xLiHal$$
(1)

The starting material LiPN<sub>2</sub> constitutes a preformed tetrahedra network made up of PN4-units, which breaks down and reforms the new network.<sup>12</sup> The high-pressure conditions suppress the elimination of N2 and preserve the formed metal nitridophosphate. Moreover, the Li halide produced during the reaction is at the same time the thermodynamic driving force and flux aiding the crystallization process of the nitridophosphate.<sup>1</sup> Flexibility and further control over stoichiometry and structure can be achieved by addition of oxides or nitrides such as Li<sub>2</sub>O, Li<sub>3</sub>N, P<sub>3</sub>N<sub>5</sub>, or PON as starting materials.<sup>2-4</sup> The targeted degree of condensation  $\kappa$ , i.e. the atomic ratio of tetrahedra centers to tetrahedra corners, influences the anionic network formed and can be controlled by the stoichiometry of the starting materials. Naturally, the low end of  $\kappa$  is 1/4, representing noncondensed tetrahedra, while the high end is determined by electrostatics. For the element combination P and N the highest  $\kappa$  is 3/5, that being the binary parent compound P<sub>3</sub>N<sub>5</sub>.<sup>13</sup>

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In this contribution we show that high-pressure metathesis may offer a systematic access to oxonitridophosphates containing a group 4 element by preparation of Zr and Hf compounds with noncondensed tetrahedra and  $\kappa = 1/4$ , namely  $Zr_{1-x}PO_{3+4x}N_{1-4x}$  and  $Hf_{1-x}PO_{3+4x}N_{1-4x}$  ( $x \approx 0.05$ ).

As these nitridophosphates have vacancies on the metal position, the end members of the O/N solid solution series, the oxophosphates Zr<sub>0.75</sub>PO<sub>4</sub> and Hf<sub>0.75</sub>PO<sub>4</sub>, are also fathomable. These are missing members of group 4 phosphates, which is curious since this group was intensively investigated because of their ion exchange and ion conductivity properties.<sup>14</sup> The subsolidus phase diagrams of the pseudobinary system ZrO<sub>2</sub>- $P_2O_5$  and several pseudoternary  $ZrO_2-P_2O_5-MO_x$  have extensively been investigated in the literature.<sup>15,16</sup> Hitherto, only three ternary structure-types, the diphosphate  $MP_2O_7$  and the orthophosphate oxide  $M_2[PO_4]_2O$  with M = Zr, Hf, as well as the chain phosphate  $Zr(PO_3)_4$  were structurally characterized.<sup>17-21</sup> ZrP<sub>2</sub>O<sub>7</sub>, among other tetravalent metal phosphates, was discussed as a H<sup>+</sup> ion conductor for fuel cells.<sup>22</sup> We were able to prepare these curious  $Zr_{0.75}PO_4$  and  $Hf_{0.75}PO_4$ compounds with the high-pressure metathesis route and so advance the chemistry of the group 4 oxophosphates.

 $Zr_{0.75}PO_4$  and  $Hf_{0.75}PO_4$  are isotypic to  $Zr_{1-x}PO_{3+4x}N_{1-4x}$ and  $Hf_{1-x}PO_{3+4x}N_{1-4x}$  ( $x \approx 0.05$ ) and crystallize in a defect variant of the ZrSiO<sub>4</sub> structure type. The structural feature of noncondensed tetrahedra is reminiscent of the important class of NASICON materials ( $Na_{1-x}Zr_2P_{3-x}Si_xO_{12}$  ( $0 \le x \le 3$ )), which are known for their ion conduction properties and nuclear waste immobilization.<sup>14,23,24</sup> Incorporation of Na into oxonitridophosphates or metastable oxophosphates through high-pressure metathesis could lead to compounds with similar properties.

In the following, we report the structures and properties of  $M_{1-x}PO_{3+4x}N_{1-4x}$  ( $x \approx 0.05$ ), and  $M_{0.75}PO_4$  (M = Zr, Hf) by means of single-crystal and powder X-ray diffraction (SCXRD, PXRD), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) spectroscopy, infrared (IR) spectroscopy, and UV–vis spectroscopy. We discuss stabilities of the compounds based on high-temperature XRD (HTXRD) and possible alternative synthesis routes of the  $M_{0.75}PO_4$  (M = Zr, Hf) to determine reasons for their late discovery.

#### EXPERIMENTAL SECTION

**Li<sub>2</sub>O.** Li<sub>2</sub>O was prepared by thermal decarboxylation of Li<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich 99.99%) under dynamic vacuum conditions ( $<10^{-3}$  mbar).<sup>25</sup> For this purpose, a fused silica tube residing in a tube furnace was loaded with a Li<sub>2</sub>CO<sub>3</sub>-filled Ag boat. The tube was connected to an Ar/vacuum Schlenk line and subsequently heated to 700 °C for 72 h in dynamic vacuum with temperature ramps set to 5 °C/min. Moisture sensitive Li<sub>2</sub>O was recovered and then stored in a glovebox. The purity of the colorless product was confirmed by PXRD to check for residual Li<sub>2</sub>CO<sub>3</sub>.

**Phosphoric Triamide.** The phosphoric triamide  $OP(NH_2)_3$  is a starting material for the synthesis of PON and was prepared by ammonolysis of phosphorus oxychloride POCl<sub>3</sub> in liquid ammonia.<sup>26</sup> A three-necked flask equipped with one connection to an inert gas/vacuum/ammonia line and one connection to an overpressure valve was dried in vacuum. Approximately 200 mL NH<sub>3</sub> (Air Liquide 5.0) was condensed into the flask with an aceton/CO<sub>2</sub> freezing mixture. Approximately 10 mL of POCl<sub>3</sub> was added dropwise through a septum into the stirred liquid ammonia. Excess ammonia was evaporated overnight and the product  $OP(NH_2)_3$  was obtained as a colorless powder in a 1:3 mixture with NH<sub>4</sub>Cl. The product was characterized by PXRD.

**a-PON.** Amorphous PON (a-PON) was prepared by condensation of  $OP(NH_2)_3$  in a constant flow of ammonia.<sup>27</sup> A fused silica tube was prepared by drying at 1000 °C for 8 h under dynamic vacuum <0.1 Pa. The above obtained 1:3 mixture of  $OP(NH_2)_3$  and  $NH_4Cl$  was loaded on a fused silica boat in an Ar-filled glovebox ( $O_2$  and  $H_2O < 1$  ppm) and conveyed into the tube furnace in an Ar counterflow via transporter. The gas flow was switched to ammonia and the starting materials fired at 300 °C for 5 h to sublimate the  $NH_4Cl$ ; then the temperature was increased to 620 °C with a 12 h dwell. All temperature ramps were set to 5 °C/min. The colorless a-PON was characterized by PXRD (check for residual  $NH_4Cl$ ) and IR.

**cri-PON.** Cristobalite phosphorus oxonitride (cri-PON) was prepared by crystallizing amorphous PON.<sup>27,28</sup> A dried fused silica tube with fused silica boat (tube furnace setup, 1000 °C for 8 h under dynamic vacuum <0.1 Pa) was loaded with a-PON. The condensation was carried out for 168 h in dynamic vacuum (<0.1 Pa) at 750 °C with temperature ramps set to 5 °C/min. cri-PON was obtained as a colorless powder and characterized by PXRD and IR.

**Oxo(nitrido)phosphates.**  $Zr_{1-x}PO_{3+4x}N_{1-4x}$  ( $x \approx 0.05$ ),  $Hf_{1-x}PO_{3+4x}N_{1-4x}$  ( $x \approx 0.05$ ),  $Zr_{0.75}PO_4$ , and  $Hf_{0.75}PO_4$  were prepared by high-pressure metathesis using a hydraulic 1000t press (Voggenreiter, Mainleus, Germany) and the multianvil technique. The setup included a modified Walker-type module (Voggenreiter) with an octahedron-within-cubes load driven by steel wedges. The here used 18/11 assembly consisted of Co-doped (7%) tungsten carbide cubes (Hawedia, Marklkofen, Germany) with truncated edges (11 mm), a  $Cr_2O_3$ -doped (6%) MgO octahedron as pressure medium (18 mm edge length), and pyrophyllite gaskets (Ceramic Substrates & Components, Isle of Wight, U.K.). The samples resided inside a h-BN crucible (Henze, Kempten, Germany), and they were heated through resistance heating with a graphite sleeve (Schunk Kohlenstofftechnik GmbH, Zolling, Germany). Additional information regarding the employed high-pressure technique can be found in the literature.<sup>29–33</sup>

Starting materials were mixed and ground in a glovebox (O<sub>2</sub> and H<sub>2</sub>O < 1 ppm). All samples were prepared by high-pressure metathesis starting from stoichiometric mixtures of ZrCl<sub>4</sub> (99.99%, Sigma-Aldrich), HfCl<sub>4</sub> (99.9%, abcr GmbH), P<sub>4</sub>O<sub>10</sub> (99.99% Sigma-Aldrich), cri-PON, and Li<sub>2</sub>O. The samples were recovered as colorless products and washed with H<sub>2</sub>O to remove the LiCl byproduct. Additional information regarding synthesis can be found in the Synthesis section.

**Spectroscopy.** A Helios Nanolab G3 Dualbeam UC (FEI, Hillsboro, OR, United States) equipped with an X-Max 80 SDD detector (Oxford Instruments, Abingdon, United Kingdom) was used for scanning electron microscopy and the recording of EDX spectra. The samples were placed on an adhesive conducting carbon foil affixed to a metal carrier and coated with carbon.

Infrared spectra were recorded on a Spectrum BX II spectrometer (PerkinElmer Waltham, MA, United States) with a DuraSampler ATRunit in the range of 650-4500 cm<sup>-1</sup>.

UV-vis spectra were recorded in reflection geometry on a V-650 UV-vis spectrophotometer (JASCO, Gross-Umstadt, Germany) equipped with a photomultiplier tube detector and a single monochromator with 1200 lines/mm. The detected spectral range was from 240 to 800 nm, scanned with a deuterium lamp (240–330 nm) and a halogen lamp (330–800 nm) with a 1 nm resolution and a scan speed of 400 nm/min. The device was controlled with the Spectra Manager II software. Samples were loaded onto a sample holder consisting of a fused silica slide and a  $BaSO_4$ -coated stamp. The baseline was recorded prior each measurement.

**Solid State NMR.** <sup>31</sup>P NMR spectra of  $M_{0.75}$ PO<sub>4</sub> (M = Zr, Hf) were recorded on a DSX Avance spectrometer (Bruker) at a magnetic field of 11.7 T. The samples were loaded into a 2.5 mm rotor made of ZrO<sub>2</sub>. The rotor was mounted on a commercial MAS probe (Bruker). Spectra were recorded at a rotation frequency of 20 kHz and at room temperature. The raw data were analyzed with the device-specific software.

**Single-Crystal Diffraction.** X-ray diffraction on single-crystals was carried out on a D8 Venture diffractometer (Bruker, Billerica, MA, United States) with a fine-focus sealed tube X-ray source. Cell determination, data reduction, and multiscan absorption correction

(SADABS), as well as calculation of planes through reciprocal space were carried out using the APEX3 software.<sup>34,35</sup> Crystals were affixed on a MicroMount (MiTeGen, Ithaca, NY, United States). The space groups were determined based on systematic absences analyzed with XPREP.<sup>36</sup> Structure solution and refinement were carried out with SHELX-97.<sup>37,38</sup> Crystal structures were visualized with VESTA.<sup>39</sup> Further details on the crystal structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: + 49-7247-808-666; e-mail: crysdata@fizkarlsruhe.de) on quoting the depository numbers CSD-433854, -433855, -433856, and -433857. CCDC 1816010–1816013 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

**Powder Diffraction.** PXRD on microcrystalline samples was carried out on a Stadi P diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) in parafocusing Debye–Scherrer geometry with Mo  $K_{\alpha 1}$  radiation. The instrument was equipped with a Ge single-crystal monochromator, singling out the  $K_{\alpha 1}$  emission line, and a MYTHEN 1K silicon strip detector (Dectris, Baden, Switzerland). Samples were loaded into glass capillaries (Hilgenberg GmbH, Malsfeld, Germany) with diameters ranging from 0.1 to 0.3 mm, depending on absorption, and a wall thickness of 0.01 mm. Diffractograms were recorded in the angular range of  $2\theta = 2-76^{\circ}$ .

Rietveld refinement was carried out with the program TOPAS-Academic V4.1.<sup>40,41</sup> Peak shapes were modeled using a fundamental parameters approach featuring a direct convolution of source emission profiles, axial instrument contributions, crystallite size, and microstrain effects. The background was handled using a shifted Chebychev polynom.

High-temperature PXRD was recorded on a Stadi P diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) with Mo  $K_{a1}$  radiation source and equipped with a graphite furnace and an image-plate position-sensitive detector. The diffractograms were recorded in the range of  $2\theta = 3-65^{\circ}$  in temperature steps of 20 K starting from room temperature to a maximum of 1000 °C. Samples were loaded into fused silica capillaries (Hilgenberg GmbH, Malsfeld, Germany) with 0.5 mm diameter and 0.01 mm wall thickness.

#### SYNTHESIS

The title compounds were prepared by high-pressure metathesis starting from the metal chlorides,  $Li_2O$ , and PON or  $P_2O_5$ , respectively. Reaction equations are as follows:

$$\operatorname{ZrCl}_4 + \operatorname{PON} + 2\operatorname{Li}_2 O \rightarrow \operatorname{ZrPO}_3 N + 4\operatorname{LiCl}$$
 (2)

$$3\text{ZrCl}_4 + 2P_2O_5 + 6\text{Li}_2O \rightarrow 4\text{Zr}_{0.75}PO_4 + 12\text{LiCl}$$
 (3)

$$HfCl_4 + PON + 2Li_2O \rightarrow HfPO_3N + 4LiCl$$
(4)

$$3HfCl_4 + 2P_2O_5 + 6Li_2O \rightarrow 4Hf_{0.75}PO_4 + 12LiCl$$
 (5)

The conditions for each reaction are listed in Table 1. All compounds were obtained as colorless and transparent single-

Table 1. Reaction Conditions for Reactions in Eqs 2 to 5

Reaction	Pressure/GPa	$Temp/^{\circ}C$	Dwell/min	Temp up/down/min
eq 2	6	1200	160	30/150
eq 3	6	1200	160	30/150
eq 4	6	1100	160	30/150
eq 5	6	1100	160	30/150

crystals large enough for XRD (Figure 1).  $Zr_{0.75}PO_4$  and  $Hf_{0.75}PO_4$  were prepared as crystallographically phase-pure materials,  $Zr_{1-x}PO_{3+4x}N_{1-4x}$  had a minor, not-quantifiable, side phase of  $ZrO_2$  and  $Hf_{1-x}PO_{3+4x}N_{1-4x}$  has an 8 wt % side phase of  $HfO_2$ .<sup>42</sup> Rietveld refinements are shown in the Supporting



Figure 1. SEM micrographs of representative crystals of (a)  $Zr_{1-x}PO_{3+4x}N_{1-4x}$  (b)  $Zr_{0.75}PO_{4}$  (c)  $Hf_{1-x}PO_{3+4x}N_{1-4x}$  and (d)  $Hf_{0.75}PO_{4}$ .

Information (Figures S1 to S4, Table S1). The thermodynamic stability of respective metal dioxides impeded the preparation of phase pure compounds, but their formation can be, to a good amount, circumvented by careful grinding of the starting materials. Structure analysis (see Structure Determination) showed that the nitrogen containing compounds both have defects on the heavy atom positions, necessitating a surplus of O for charge balancing and thus leading to sum formulas  $M_{1-x}$ PO<sub>3+4x</sub>N<sub>1-4x</sub> (x  $\approx$  0.05, M = Zr, Hf). Infrared spectroscopy did not indicate the presence of N-H or O-H bonds (Figure \$5). EDX of the compounds showed that the experimentally determined composition is in good agreement with the theoretical values: experiment/theory  $\begin{array}{l} Zr_{1.17(1)}P_{1.08(7)}O_{2.99(17)}N_{0.72(23)}/Zr_{0.95}P_{1}O_{3.2}N_{0.8} \ (\mbox{three points}), \\ Zr_{0.85(6)}P_{0.85(9)}O_{4.04(15)}/Zr_{0.75}P_{1}O_{4} \ (\mbox{three points}), \end{array}$  $Hf_{1.08(10)}P_{1.01(4)}O_{3.11(16)}N_{0.72(13)}/Hf_{0.95}P_1O_{3.2}N_{0.8}$  (nine points), Hf<sub>0.87(10)</sub>P<sub>0.94(8)</sub>O<sub>3.94(16)</sub>/Hf<sub>0.75</sub>P<sub>1</sub>O<sub>4</sub> (eight points). EDX and single-crystal analysis indicate that the amount of Zr/Hf and N/ O incorporated in  $M_{1-x}PO_{3+4x}N_{1-4x}$  seems to favor a structure with vacancies on the heavy atom position. We found no experimental evidence for the existence of the end members ZrPO<sub>3</sub>N and HfPO<sub>3</sub>N. This could have electrostatic causes, in which for energy minimization vacancies are required. Singlecrystal diffraction and EDX, however, are not methods for generating statistics; hence, the real compositional variance can only be estimated. The composition certainly varies to some degree around the postulated value of  $x \approx 0.05$ , and in domains the end members ZrPO<sub>3</sub>N and HfPO<sub>3</sub>N might be present. The analysis of this, however, is beyond the scope of this report.

#### STRUCTURE DETERMINATION

The crystal structures of all compounds were solved and refined from single-crystal data. Crystallographic data is summarized in Table S2, atom positions in Table S3, lists of anisotropic displacement parameters, bond lengths, and angles can be found in the Supporting Information (Tables S4–S6). The structures were solved in space group  $I4_1/amd$  (no. 141), determined from systematically absent reflections, yielding the positions of all heavy atoms including P. O and, respectively, N were determined through difference Fourier maps. The occupancy of the single Zr and Hf positions in  $M_{1-x}PO_{3+4x}N_{1-4x}$  ( $x \approx 0.05$ , M = Zr, Hf) was freely refined and the O/N occupancy adjusted to maintain charge neutrality. The  $M_{0.75}$ PO<sub>4</sub> structures were tested for additional vacancies on the P and M positions; however, none were found, and therefore, both occupancies were fixed to 1 and 3/4, respectively (details in Supporting Information). As the heavy atom positions of all products are not fully occupied, they might form an ordered vacancy distribution. Such an ordering would require either a lowering of the space group symmetry, as only one Zr/Hf Wyckoff-position exists in I41/amd (no. 141), or an enlarged unit cell. Reconstructed planes through reciprocal space (Figures S6 to S9) indicate neither the existence of superstructure reflections nor reflections breaking the systematic absences, as would be required for the maximal translationengleiche subgroups of  $I4_1/amd$  (no. 141). Hence, a random distribution of vacancies was assumed. The structure models with a random distribution of vacancies were also corroborated by <sup>31</sup>P solid state NMR measurements carried out on the  $M_{0.75}$ PO<sub>4</sub> compounds (Figure S10).

# STRUCTURE DISCUSSION

All title compounds crystallize in the  $ZrSiO_4$  structure-type, space group  $I4_1/amd$  (no. 141), albeit being defect variants as the heavy atom positions are not fully occupied. The crystal structure comprises noncondensed  $P(O/N)_4$  tetrahedra, as illustrated in projection along [100], alternatingly pointing upand downward (Figure 2). The tetrahedra are separated by



**Figure 2.** Unit cell of the Zr and Hf orthophosphates. Figure based on structure model of  $Zr_{1-x}PO_{3+4x}N_{1-4,x^{2}}$  with metal atoms in green, P in black and N in orange: (a) random orientation of the unit cell; (b) projection along [100]. Ellipsoids are set to a 90% probability level.

heavy atoms, which are coordinated in a  $M(O/N)_8$  bisdisphenoid (also called dodecadeltahedron, Johnson solid J<sub>84</sub>, Figure 3).<sup>43</sup> The bisdisphenoid is common in structures with noncondensed tetrahedra and has been observed in the room temperature modification of AgClO<sub>4</sub> as well as anhydrite



**Figure 3.** Heavy-atom  $M(O/N)_8$  coordination polyhedron based on structure model of  $Zr_{1-x}PO_{3+4x}N_{1-4x}$ , with metal atom in green and N in orange: (a) polyhedron in random orientation; (b) polyhedron in projection along the  $\overline{4}$  rotoreflection. Ellipsoids are set to a 90% probability level.

CaSO<sub>4</sub> and scheelite CaWO<sub>4</sub>.<sup>44-46</sup> A mathematical bisdisphenoid is a deltahedron with symmetry  $D_{2d}$  in Schönflies notation and vertex symbol  $(3^4)_4(3^5)_4$ ; in the  $M(O/N)_8$ polyhedra of presented orthophosphates this symmetry is retained (Figure 3b) but two different M-(O/N) distances lead to irregular triangles as faces of the polyhedra.<sup>47</sup>

A comparison of the title compounds with  $ZrSiO_4$  and  $HfSiO_4$  shows that the Hf compounds have a smaller unit cell than their Zr counterparts (Figure 4).<sup>48,49</sup> This shrinkage is due



**Figure 4.** Comparison of lattice parameters *a* and *c*, unit cell volumes *V*, and P-(X) and M-(X) (X = O/N) distances of all title compounds as well as  $ZrSiO_4$  and  $HfSiO_4$ .<sup>48,49</sup> Cell parameters of the title compounds were extracted from Rietveld refinement and interatomic distances from single-crystal refinement. Standard deviations are displayed for interatomic distances, not for lattice parameters as they are too small to be visualized.

to the increased relativistic contraction of the 5d Hf atoms compared to the lighter 4d Zr atoms, resulting in slightly smaller Hf atoms.<sup>50</sup> Chemically, Hf and Zr are very similar, unlike, e.g. Mo and W; the relativistic contraction and the shell-structure expansion cancel each other out, which might explain why Hf and Zr adopt the same structure-type.<sup>51</sup> Since the heavy-atom positions in  $M_{0.75}$ PO<sub>4</sub> are occupied to 3/4, their unit cell volume is expectedly smaller than that of the oxonitridophosphates. The P–(O/N) bond lengths are longer for the nitrogen containing compounds than in the pure oxophosphates, but all bond lengths are shorter than the respective Si–O interatomic distances of zircon and hafnon.

The P–(O/N) bond lengths found here are in good agreement with values found in  $\beta$ -K<sub>2</sub>SO<sub>4</sub>-type Sr<sub>2</sub>PO<sub>3</sub>N (d(P–(O/N)) = 1.569–1.574).<sup>52</sup> For the M–(O/N) distances no trend can be postulated, and the values of the two different distances range from 2.135 to 2.163 Å and from 2.250 to 2.264 Å, respectively.

## THERMAL PROPERTIES

High-temperature PXRD diffractograms (Figures S12 to S15) were recorded to a maximum temperature of 1000 °C to investigate the thermal stability of the compounds in air. The oxophosphates  $M_{0.75}PO_4$  seem to undergo a phase transformation to ambient pressure polymorphs with the same composition at ca. 900 °C for  $Zr_{0.75}PO_4$  and at ca. 780 °C for  $Hf_{0.75}PO_4$ . The diffraction pattern of the  $Zr_{0.75}PO_4$  phase transformation matches a unit cell reported by Alamo et al.

reported for Zr orthophosphate Zr<sub>2.25</sub>(PO<sub>4</sub>)<sub>3</sub>. This Zr<sub>2.25</sub>(PO<sub>4</sub>)<sub>3</sub> was reported to enter the NASICON structure-type as the unit cell is similar to that of NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (Figure S16).<sup>21</sup> The phase transformation of Hf<sub>0.75</sub>PO<sub>4</sub> yields a similar powder pattern (Figure S17), but no corresponding Hf<sub>2.25</sub>(PO<sub>4</sub>)<sub>3</sub> structure has been reported. Since the unit cell reported for Zr<sub>2.25</sub>(PO<sub>4</sub>)<sub>3</sub> also matches the reflection pattern after the phase transformation, a similar structure can be assumed.

While no decomposition was observed for the  $Hf_{1-x}PO_{3+4x}N_{1-4x}$  up to 1000 °C, the oxonitridophosphate  $Zr_{1-x}PO_{3+4x}N_{1-4x}$  decomposes at ca. 680 °C. Most of the diffraction pattern can be explained by the  $Zr_{2.25}(PO_4)_3$  reference; however, several reflections could not be assigned to any known phase (Figure S18). From the chemical composition the unknown phase should be rich in Zr, but the pattern did not match that of  $ZrO_2^{.42}$ .

#### OPTICAL PROPERTIES

The UV-vis spectra recorded for each compound reveal valence to conduction band transitions in the UV range (Figure S19). To obtain an estimate of the optical band gap, the reflectance spectra were transformed into the Kubelka–Munk function and plotted in a Tauc-plot (Figure 5).<sup>53,54</sup> A direct



**Figure 5.** Tauc-plots of all compounds, generated from UV–vis reflectance data. Kubelka–Munk function in black, linear regression (blue) fit to data points highlighted in red. Special case for  $Hf_{0.75}PO_4$  as two slopes are discernible; two regression lines (blue and green) were fit to the data points (red and orange) yielding adsorption onset values of 3.6 and 4 eV, respectively.

band gap was assumed for the structures. A linear regression was fit to the regions of steep slope and the estimated band gap value read off at the *x*-axis intersection. The values for the  $M_{1-x}PO_{3+4x}N_{1-4x}$  (M = Zr, Hf) are  $E_g \approx 3.5$  and 4.3 eV, respectively, while  $Zr_{0.75}PO_4$  has a value of  $E_g \approx 4.2$  eV. The band gap of Hfr<sub>0.75</sub>PO<sub>4</sub> cannot unambiguously be derived since the UV–vis spectra shows no clear beginning of the valence to conduction band transition (Figure S19d), which leads to a Kubelka–Munk function with an additional point of inflection in the region of steepest slope (Figure 5, bottom). Two different slopes are discernible, both leading to different values

of  $E_{gr}$  3.6 and 4 eV, respectively. This absorption might not only be caused by the valence to conduction band transition but could also be influenced by local defects. Hence, a true optical band gap cannot be derived here, only the beginning of absorption, which is at  $\approx$ 3.6 eV.

#### ALTERNATIVE SYNTHESIS METHODS

Metathesis reactions were successfully applied in the synthesis of temperature labile compounds of, e.g., metal borides, nitrides, and carbides.<sup>55</sup> The energy for the product formation is generated through the exothermic nature of the metathesis reaction, allowing for lower furnace temperatures. Since Hf<sub>0.75</sub>PO<sub>4</sub> and Zr<sub>0.75</sub>PO<sub>4</sub> are ternary phosphates they might be accessible without applying high pressures. Analogous metathesis reactions were therefore carried out in alumina crucibles in sealed Ar ampules at 700 °C. This temperature was chosen since the HTXRD data indicate that both phosphates do not start to undergo a phase transformation at that temperature. The reactions, however, did not yield the desired orthophosphate as  $M_2(PO_4)_2O$  ( $M = Hf_1$ , Zr), and unidentified side phases were formed.<sup>19</sup> Hence, formation of the orthophosphate, with its defect ZrSiO<sub>4</sub> structure, seemed to be stabilized under high-pressure conditions. As mentioned in the HTXRD section, the phosphates undergo a phase transformation to the ambient pressure form of  $Zr_{2,25}(PO_4)_3$ .<sup>21</sup> Hence the oxophosphates reported here might be the high-pressure polymorphs of this structure-type and metastable under ambient pressure conditions. Hence they were not previously discovered despite the thorough investigation of the group 4 phosphates. Thus high-pressure metathesis opens a route to compounds that are thermally labile and potentially metastable at ambient pressures.

#### CONCLUSION

The preparation of the oxonitridophosphates with group 4 metals comprising noncondensed  $P(N/O)_4$  tetrahedra,  $M_{1-x}PO_{3+4x}N_{1-4x}$  (M = Zr, Hf) shows that high-pressure metathesis can grant a systematic access to this class of compounds. Naturally, more types of anion network have to be prepared to underline the capability of the high-pressure metathesis route.

Moreover, high-pressure metathesis could be a viable route to unknown oxophosphates, as shown with the preparation of  $Zr_{0.75}PO_4$  and  $Hf_{0.75}PO_4$ . The latter are inaccessible by ambient pressure synthesis methods and are probable high-pressure polymorphs of the  $M_{2.25}(PO_4)_3$  phases crystallizing in the NASICON structure-type.  $Zr_{0.75}PO_4$  and  $Hf_{0.75}PO_4$  have, most likely, not been discovered before since they are metastable at ambient pressures and could not be prepared without highpressure techniques. Hence, high-pressure metathesis could also be used to target metastable systems of oxophosphates, which were previously only accessible via kinetic control of ambient pressure synthesis methods.

The orthophosphates reported here are an intriguing starting point for the search for ion conduction properties within the group 4 (nitrido)phosphates, as are known from the structurally related class of NASICON materials.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00373.

Rietveld refinement data, infrared spectroscopy, crystallographic tables, details on structure determination, NMR measurements, high-temperature powder diffraction, UV–vis spectroscopy (PDF)

#### **Accession Codes**

CCDC 1816010–1816013 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: wolfgang.schnick@uni-muenchen.de.

ORCID <sup>©</sup>

Wolfgang Schnick: 0000-0003-4571-8035

Notes

The authors declare no competing financial interest.

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