PrVO₄ under High Pressure: Effects on Structural, Optical and Electrical Properties

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Abstract
In pursuit of a systematic characterization of rare-earth vanadates under compression, in this work we have studied the phase behavior of zircon-type orthovanadate PrVO₄ under high pressure conditions, up to 24 GPa, by means of powder x-ray diffraction. We have found that PrVO₄ undergoes a zircon to monazite transition around 6 GPa, confirming previous results found on Raman experiments. A second transition takes place above 14 GPa, to a BaWO₄-II -type structure. The zircon to monazite structural sequence is an irreversible first-order transition, accompanied by a volume collapse of about 9.6%. Monazite phase is thus a metastable polymorph of PrVO₄. The monazite- BaWO₄-II transition is found to be reversible instead and occurs with a similar volume change. Here we report on the axial and bulk compressibility of all phases. We also compare our results with those for other rare-earth orthovanadates. Finally, by means of optical-absorption experiments and resistivity measurements we determined for the first time the effect of pressure in the electronic properties of PrVO₄. We found that the zircon-monazite transition produces a collapse of the band gap and an abrupt decrease of the resistivity. Reasons for this behavior are going to be discussed.
1. Introduction

Due primarily to their technological and theoretical relevance, REVO₄ rare-earth orthovanadates (with RE=trivalent rare-earth atom) are currently receiving a great deal of attention. In fact, as a consequence of their optical and luminescent properties, many of these materials are suitable for real-world applications, such as photocatalysts for the elimination of some organic pollutants and dyes,⁴⁻⁶ as host materials for laser applications, luminescent emitters, thermophosphors and non-linear optics.⁴⁻¹⁰ These compounds are also challenging from the point of view theory and basic research, especially in the field of High-Pressure Physics. In first approximation, zircon REVO₄ follow a well-defined structural pathway under high-pressure conditions. Indeed, NdVO₄ and compounds with larger RE cations tend to transform to a monoclinic monazite phase under pressure, while SmVO₄ and compounds with smaller cations experiment a transition to a scheelite structure.¹¹,¹² Nonetheless, this general trend can be altered by experimental conditions, as it has been established primarily in quasi-hydrostatic conditions, i.e. using the most common liquid pressure transmitting media (PTMs) such as silicon oil, methanol:ethanol or methanol:ethanol:water (ME, MEW).¹³ Alternative PTM choices can alter significantly the behavior of REVO₄. For example, it has been shown recently by Marqueño et al. that NdVO₄ follows a zircon-scheelite-fergusonite transition sequence upon compression in a hydrostatic pressure medium (He).¹⁴ For HoVO₄ the transition pressure from zircon to scheelite is almost halved when compressing it in a non-hydrostatic PTM. Moreover a further phase transition, which is not observed in quasi-hydrostatic conditions, is found above 20 GPa.¹⁵ On the other hand, the behavior of cerium vanadate CeVO₄ is somewhat erratic, showing signs of an unstable equilibrium. This compound can indifferently transform from zircon to a scheelite or a monazite structure in a non-hydrostatic medium. On the contrary, it shows a well-defined zircon-monazite transition when using a highly hydrostatic PTM. Further, mixed vanadates such as Sm₀.₅Nd₀.₅VO₄ have an even more peculiar behavior, as the first phase transition sees the coexistence of two different phases, which has been shown not being due to the presence of crystalline domains with excess of Nd or Sm.¹⁶ All these examples show the rich phenomenology that can be presented during the systematic investigation of RE vanadates and confirm the need for further insights in this area. Here we present a comprehensive study of zircon-type PrVO₄ under high pressure conditions, up to about 24 GPa by means of powder X-ray diffraction, optical absorption and resistivity measurements. This compound, as SmVO₄, is being investigated for its use as a photo-degradant for organic dyes.¹⁷ On the other hand, the number of high-pressure studies on PrVO₄ under high pressure remains still scarce. To the best of our knowledge, the only previous work is the one by Errandonea et al., which reported the presence of a transition from zircon to a monazite phase by means of Raman spectroscopy.¹⁸ Using powder samples with synchrotron radiation we have been able to find two different phase transitions for PrVO₄ in the range 1 bar – 24 GPa. Firstly, we confirmed the results obtained by Errandonea et al. from Raman measurements,¹⁸ i.e. a zircon-monazite transition is identified above 6 GPa. This transition implies an atomic rearrangement and a coordination change of the Pr³⁺ ion from 8 to 9, together with a large volume collapse, of about 9.6%. Upon pressure increase, a second phase transition occurs, from the monazite to a BaVO₄-II type structure, which belongs to the same space group of monazite but has 8 formula units per unit cell, instead of 4 as in zircon and monazite. In addition, optical-absorption and resistivity measurement found drastic changes induced by pressure in the electronic properties of PrVO₄, which can be associated to the zircon-monazite transition. These findings will be
discussed in comparison with the behavior of other lanthanide orthovanadates under compression.

2. Experimental Details

PrVO$_4$ single crystals were synthetized by the flux method, following a process that has been described elsewhere in detail for analogous REVO$_4$ orthovanadates.$^{19}$ The obtained samples were optically clear and up to 10 mm long.

High-pressure angle-dispersive powder X-ray diffraction (P-XRD) experiments were performed at room temperature (RT) employing a membrane diamond-anvil cell (DAC), with diamond culets of 400 μm. For our experiments, selected crystals, with no flux inclusions, were chose and carefully grinded down to a fine powder. The powder was loaded in a 180 μm hole drilled on a stainless-steel T301 gasket pre-indented to a thickness of 40 μm. Copper powder (Cu) was used as the pressure gauge and a methanol:ethanol:water 16:3:1 (MEW) mixture was used as the pressure-transmitting medium (PTM). Experiments were performed at the BL04-MSPD of ALBA Synchrotron with a monochromatic X-ray beam (λ = 0.4246 Å) focused to a 20 μm × 20 μm spot (FWHM).$^{20}$ XRD patterns were collected with a Rayonix CCD detector. Structural analyses were performed with GSAS-II and MAUD, using the Le Bail method.$^{21,22}$ Visualization of crystal structures has been done with VESTA.$^{23}$ EosFit7-GUI has been used to calculate the bulk modulus by fitting the pressure-volume data with the Birch-Murnaghan equation of state (EOS).$^{24}$

For optical measurements we used 10-μm thick platelets cleaved from the single-crystals. The experiments were performed in a membrane-type DAC with diamond culets of 500-μm. The pressure medium was also 4:1 ME. In this case the ruby scale was used to determine pressure.$^{25}$ Measurements were carried out with the sample-in sample-out method.$^{26}$ Resistivity measurements up to 10 GPa were carried out using an opposed Bridgman-anvil setup.$^{27}$ The pressure was determined by calibrating the hydraulic pressure of the press against known phase transitions.$^{28}$ A sintered powdered sample, made from the sample used in Ref. 18, with 3 mm × 3 mm × 0.1 mm dimensions was used in this experiment. The measurements were carried out in a four-point configuration.

3. Results and Discussion

As most REVO$_4$ vanadates (except LaVO$_4$), PrVO$_4$ crystallizes naturally in a zircon structure (S.G. 141, $I4_1/amd$, Z=4), in which the vanadium atom is surrounded by four oxygen atoms in a tetrahedral coordination and the trivalent Pr cation is eight-fold coordinated with oxygen atoms, forming PrO$_8$ bidispensoids (Figure 1). Unit-cell parameters for zircon PrVO$_4$ at ambient conditions, as measured by powder XRD, are $a = 7.3625(2)$ Å, $c = 6.4614(4)$ Å, with a volume $V = 350.26(2)$ Å$^3$. These values are in good agreement with previous reports, from which they differ by less than 0.1% (Table 1).$^{29}$
Figure 1. Zircon structure of PrVO₄. The coordination polyhedra of Pr and V are in yellow and red, respectively.

| zircon PrVO₄          |       |       |
|-----------------------|-------|-------|
|                       | a (Å) | c (Å) | V (Å³) |
| This work             | 7.3625(2) | 6.4614(4) | 350.26(2) |
| literature²⁹          | 7.3631(1) | 6.4650(1) | 350.5(7) |

Table 1. Cell parameters and atomic positions for zircon PrVO₄, as reported in Ref. 29. Wyckoff positions are Pr (4a), V(4b), O(16h).

In Figure 2a we show the powder XRD patterns for PrVO₄ at selected pressures. Patterns below 6.2 GPa are correctly indexed by the zircon structure and show little changes with pressure, such as the usual shift towards higher values of 2θ due to the shrinking unit cell. On the other hand, at 6.2 GPa sudden changes appear, because of the onset of a phase transition. The new phase can be indexed in the monazite structure (S.G. 14, P2₁/n, Z=4), with unit-cell parameters \( a = 6.9930(8) \) Å, \( b = 7.1796(7) \) Å, \( c = 6.6311(8) \) Å and \( \beta = 104.60(1) \)° \( (V = 322.2(8) \) Å³). This structure is represented in Fig. 3; it consists of PrO₉ polyhedra and VO₄ tetrahedra. As the monazite phase is stable upon pressure release, these values have been obtained at 0.4 GPa, the residual pressure in our DAC. This is in full agreement with previous results obtained for PrVO₄.¹⁸ The range of stability of the monazite phase is limited at increasing pressure, as new features arise in the XRD patterns above 6.8 GPa. These are most evident in the low 2θ range: a peak around 4.5° becomes weaker, while new ones appear around 7° and 9° (Figure 2b). This is the indication of the onset of a new phase transition to a post-monazite phase. The superposition of the two phases only allows reliable Le Bail refinements at higher pressure, starting around 14.45 GPa. As one can see in Figure 2a, the Bragg peaks become broader after the first transition, probably due to strain in the crystal grains and a to large volume collapse (more details in the following). The quality of our XRD patterns above 6.2 GPa does not allow for a full Rietveld refinement. Upon comparison with the literature, we found that a good candidate
for the post-monazite phase is the monoclinic BaWO$_4$-II structure (S.G. 14, $P2_1/n$, Z=8), which belongs the same space group of monazite but has a unit-cell twice as large (Figure 4). An analogous transition has in fact been reported before for monoclinic LaVO$_4$.\textsuperscript{10} The BaWO$_4$-II structure is able to explain all the peaks of the post-monazite phase, as shown in Figure 5, where some remnants of the monazite phase are still visible. Above 10 GPa, the diffraction peaks are broadened, due to the loss of hydrostaticity of the PTM.\textsuperscript{13} Reliable cell parameters for the BaWO$_4$-II phase could be only obtained at higher pressure, around 14.45 GPa (see Figure 5), and are $a = 11.557(7)$ Å, $b = 6.522(7)$ Å, $c = 6.847(7)$ Å and $\beta = 90.71(1)^\circ$ ($V = 516.1(8)$ Å$^3$).

**Figure 2.** a) XRD patterns for PrVO$_4$ at different pressures (open red circles). The pressure $P$ is indicated in GPa at the right of the plot; Le Bail refinements (black lines) are shown for the zircon phase at ambient pressure, and the monazite at 6.2 GPa. Green lines: residuals. Blue ticks: Bragg reflections; b) XRD patterns showing new peaks (indicated by arrows) arising with increasing pressure above 6.80 GPa. Asterisks are shown in proximity of the Cu peaks.
Figure 3. Unit cell of monazite PrVO₄. The coordination polyhedra of Pr and V are in yellow and red, respectively. Atomic positions were taken from Ref. 18.

Figure 4: Crystal structure of the BaWO₄-II phase of PrVO₄. The coordination polyhedra are indicated: yellow, Pr; red, V. Small red spheres are oxygens.
Figure 5. XRD patterns for PrVO$_4$ at 14.45 GPa (open red circles). Black lines: Le Bail refinement; green lines: residuals; blue (magenta) ticks: Bragg reflections for the BaWO$_4$-II (monazite) structure. Asterisks are shown in proximity of the Cu peaks.

The BaWO$_4$-II phase is stable up to the maximum pressure reached in our experiment, around 23.4 GPa. As said, upon pressure release the system recovers the monazite phase, which is found to be stable even near ambient pressure (Figure 6). As shown in previous reports, monazite PrVO$_4$ is confirmed to be a metastable polymorph of PrVO$_4$.$^{18}$

Figure 6. XRD patterns at pressure release, showing the gradual recovery of the monazite phase form BaWO$_4$-II structure. The pressure $P$ is indicated in GPa at the right of the plot; Le Bail refinements (black lines) are shown for the BaWO$_4$-II-type phase at 23.4 GPa and for the monazite phase at pressure release, 0.4 GPa. Green lines: residuals. Blue ticks: Bragg reflections. Asterisks are shown in proximity of the Cu peaks.
Now we will discuss the axial compressibility of each one of these structures. This is defined as \( k_s = -\frac{s}{s_0} \frac{\partial s}{\partial P} \), where \( s \) is one of the cell parameters (\( a, b \) or \( c \)), \( s_0 \) its value at ambient pressure and \( P \) is the pressure. The values of the compressibility of each axis for the different phases are reported in Table S1 (sup. Material) and were obtained by performing linear fits on the data points in Figure 4. Notice that the unit-cell parameters obtained for monazite-type PrVO\(_4\) agree well with those obtained from quenched samples in a large volume press (open diamonds in Figure 7).\(^{18}\)

![Figure 7](image_url)

**Figure 7.** Experimental cell parameters of the zircon (squares), the monazite phase (circles) and the fergusonite phases (triangles) as a function of pressure. Open diamonds are the parameters from Ref. 18. Red lines are the lineal fits of the experimental values used to calculate the axial compressibility. Open circles are data for monazite taken during pressure release. Crossed circles for monazite are data not used in the fits (see main text).

The axial compressibility of the zircon phase is strongly anisotropic (Figure 7), as it is larger along \( a \) than along \( c \), with \( k_a = 3.1(1)\times10^{-3} \) GPa\(^{-1} \), \( k_c = 1.29(8)\times10^{-3} \) GPa\(^{-1} \). The anisotropy of the zircon phase is not unusual for REVO\(_4\), being due to their polyhedral arrangement, and in the case of PrVO\(_4\) is in line with previous reports.\(^{11,14,31}\) In zircon PrVO\(_4\) the volume of the VO\(_4\) units is almost 11 times lower than that of the PrO\(_8\) polyhedra, implying that at first order the compressibility is dominated by the changes of PrO\(_8\) molecular units. In the zircon phase, these units lie in zig-zag chains along [100] and [010] and are stacked along [001], separated by the scarcely compressible VO\(_4\) tetrahedra (Figure 1). This explains why PrVO\(_4\) is preferentially compressed along [100] (and [010]) than along [001]. The monazite phase has a strongly anisotropic compressibility too, with the \( a \) and \( b \) axes being up to 1.5 times more compressible than the \( c \) axis (Table S1). In Table S1 for completeness we also include the
compressibility of the $\beta$ angle, $k_\beta$ for both monocline structures: $\beta$ angle decreases with pressure for the monazite, while it has a slightly increasing trend for the BaWO$_4$-II phase (Figure 8 and Table S1). Also, the $\beta$ angle of the monazite phase suffers a discontinuity at the transition, after pressure release. We believe that this is due to stress in the crystal grains after two subsequent phase transitions. This also causes the broadened peaks for monazite in Figure 2a. In our refinements we have assumed for monazite PrVO$_4$ the atomic position reported by Errandonea et al.,$^{18}$ so the monazite unit-cell has the layout shown in Figure 3. Also, given that monazite is stable near ambient pressure, the cell parameters of monazite for $P < 6.2$ GPa have been taken in account in our calculations. A qualitatively similar behavior with regard to its anisotropic compressibility has been found for the axial compressibility of monazite-type LaVO$_4$,$^{12}$ monazite-type CeVO$_4$, and monazite-type phosphates.$^{32,33}$ It has to be noted that in the fits for the monazite structure we neglected the values of the parameters at 12.7 GPa, as the superposition of the monazite and the BaVO$_4$-II phases made them less reliable.

Finally, a strong decrease of the axial compressibility is found for the BaWO$_4$-II structure, which anyway is more balanced than that of monazite, with the $b$ and $c$ axis having roughly the same compressibility and the $a$ axis being slightly stiffer. In addition, the $\beta$ angle of the BaWO$_4$-II structure is less affected by pressure than the angle of monazite (Table S1). As we will see in the following, another volume collapse takes place at the second transition, thus increasing the packing of the structure. This globally limits the compressibility of the post monazite phase.

![Figure 8](image_url)  
**Figure 8.** Trend of the $\beta$ angle of monazite and BaWO$_4$-II-type as a function of pressure. Open circles for monazite are data taken during pressure release. The diamond indicates the angle of monazite PrVO$_4$ at ambient pressure as reported in Ref. 18.
Figure 9. Volume as a function of pressure for the different phases of PrVO₄. Red lines are the fit of the Birch-Murnaghan EOS. Full symbols indicate measurements taken during pressure release. Crossed data have not been taken in account for the EOS fits (see main text).

In the following we will comment on the EOS of PrVO₄. Pressure-volume (P-V) data are shown in Figure 9. A volume collapse of about 9.6% (measured as the difference between the equations of state) is detected at the onset of phase transition (P = 6.2 GPa) which, together with the irreversibility of the transition, confirms its first-order nature. This is consistent with previous reports for the zircon-scheelite transition in other rare-earth orthovanadates.¹¹ The bulk moduli of all polymorphs have been estimated by fits of the pressure-volume data with a 2nd order Birch-Murnaghan EOS (Table 2). As commented before, the data point at 12.7 GPa has been neglected in the data analysis and is shown in Figure 9 only for completeness. For zircon PrVO₄, the initial volume V₀ and the bulk modulus B₀ resulting from the fits are V₀=350.4(3) Å³, B₀=120.3(3) GPa. The calculated ambient-pressure volume is in good agreement with the experimental value. Similar bulk moduli have been found in the isostructural CeVO₄, TbVO₄ and TmVO₄ vanadates.¹¹,³⁴ Under compression in non-hydrostatic media most zircon REVO₄ vanadates have higher bulk moduli, often above 130 GPa.¹¹ Zircon PrVO₄, together with TmVO₄, is thus one of the softest vanadates. This is true also for the monazite phase, which has a bulk modulus of 95(6) GPa. This is an extremely low value, as a bulk modulus of less than 100 GPa has only been found in the low-pressure phase of monazite-type LaVO₄.¹¹ It is
reasonable to compare our value of $B_0$ to those of the low-pressure phase of monoclinic LaVO$_4$, as it has been calculated using also using the cell parameters of the monoclinic PrVO$_4$ in the low-pressure range (i.e. at pressure release). The low-symmetry of the monoclinic phases allow structural distortion which are not permitted in more symmetric structure. For this, VO$_4$ units in monoclinic REVO$_4$ also contribute to the volume reduction of the unit cell, unlike what happens in zircon or scheelite. The low bulk modulus of the high-pressure phases of PrVO$_4$ observed here might be thus a consequence of the more efficient packing of the monoclinic structures. There could also be other reasons behind the high compressibility of the first HP phase of PrVO$_4$. This could be related to the broadening of the Bragg peaks after the transition, which makes less accurate the determination of unit-cell parameters. Peak broadening in turn are caused by the stress due to the large volume collapse of the phase transition. Further experiments, using Ne or Ne as the PTM, are needed to clarify this issue. We also found a huge volume collapse also at the monazite-BaWO$_4$-II transition, of about 9.18%. This variation comes with a change in the coordination of Pr (from 9 to 10) and V (from 4 to 6), which increase the packing of the structure. Following it, the post-monazite phase has a high bulk modulus of 147(6) GPa. This value is in full agreement with the bulk modulus of the post-monazite phase of LaVO$_4$, which also occurs with a similar volume collapse (around 8%). This finding suggests that the BaWO$_4$-II phase may be the post-monazite structure of other vanadates too. For instance, BaWO$_4$-II has been proposed as the post-monazite phase for NdVO$_4$ on the basis of theoretical simulations, with a similar calculated value for the bulk modulus. In this respect, we know that the transition sequence in REVO$_4$ vanadates is determined, in the first instance, by the size of the RE trivalent cation. NdVO$_4$ and vanadates with bigger cations follow the zircon-monazite-post-monazite sequence, while SmVO$_4$ and vanadates with smaller cation are expected to undergo a zircon-scheelite-fergusonite sequence. Sm and Nd are thus considered the boundary that determines the behavior of the REVO$_4$ compounds under high-pressure. On the other hand, in proximity of the Sm-Nd limit or for compounds with a RE cation with an effective size halfway between Nd and Sm (mixed vanadates), the equilibrium is unstable and may be shifted due either to experimental conditions or to energetic reasons. For instance, NdVO$_4$ under hydrostatic compression follows the zircon-scheelite-fergusonite sequence, while mixed vanadates such as Sm$_{0.5}$Nd$_{0.5}$VO$_4$ follows an even more peculiar path, with scheelite and monazite coexistence in a limited pressure range. The ionic radii of Pr$^{3+}$ and Nd$^{3+}$ is similar (0.99 vs. 0.983 Å respectively), hence it is reasonable to argue that the behavior of PrVO$_4$ may change with different experimental conditions. The confirmation of our hypotheses will thus come from high-pressure experiments for PrVO$_4$ in a hydrostatic medium, such as He, and from ab initio enthalpy simulations, which at the moment are not available.

|            | $V_0$ (Å$^3$) | $B_0$ (GPa) | $B_0$ (implied) |
|------------|--------------|-------------|----------------|
| zircon     | 350.4(3)     | 120(3)      | 4              |
| monazite   | 321(4)       | 95(6)       | 4              |
| BaWO$_4$-II| 561(4)       | 147(6)      | 4              |

Table 2. Parameters of the 2nd order Birch-Murnaghan EOS of PrVO$_4$. $V_0$, volume at ambient pressure, $B_0$ bulk modulus, $B_0'$ first derivative of bulk modulus. To allow meaningful direct comparisons, a 2nd order EOS was used for all the phases.
We will now discuss the influence of pressure on the electronic properties of PrVO$_4$. In Fig. 10 we present the results of optical-absorption measurements. As can be seen in the figures, PrVO$_4$ has a wide band gap which can be assigned to a direct transition as in other zircon-type vanadates. A value of 3.74(2) eV is obtained for the band-gap energy when a Tauc analysis is applied. This approach is known to work well in this family of oxides. The obtained band-gap energy is very similar to that of other zircon-type vanadates. As can be seen in Fig. 10, up to 5.3 GPa the absorption edge (and consequently the band-gap energy) of PrVO$_4$ is little affected by pressure. However, in a subsequent compression step we found an abrupt red shift of the band gap. This change can be correlated with the zircon-monazite transition detected by XRD at a similar pressure. A similar behavior has been observed at the same transition in NdVO$_4$. Upon further compression, the absorption edge slightly redshifts with pressure up to 11.4 GPa. Beyond this pressure several cracks started to develop in the crystal, which in case of further developing would preclude the performance of absorption measurements. Therefore, we decided to release pressure. We think the cracks are related to precursor defects of the second phase transition observed at a higher pressure. Under decompression we observed the phase transition is not reversible.

![Figure 10](image)

*Figure 10.* Absorption spectra of PrVO$_4$ at different pressures.

From our experiment we obtained the pressure dependence of the band-gap energy. They are shown in Fig. 11. In the low-pressure phase, the band gap slightly opens with pressure with a pressure coefficient of $dE_g/dP = 4(2)$ meV/GPa. This is very similar to what happens in NdVO$_4$ and related vanadates. The small increase of the band-gap with pressure is related to the decrease of the V-O distances with pressure. It is known that the top of the valence band and the bottom of the conduction band in zircon-type vanadates are dominated by V 3d and O 2p states. The decrease of the V-O distance with pressure will enhance the repulsion between

...
bonding and anti-bonding states, causing the observed opening of the gap. The VO₄ tetrahedron is known to be very uncompressible. This is the reason why the band gap changes little with pressure. As observed in NdVO₄, at the zircon-monazite transition there is an abrupt decrease of the band gap, whose energy value is 3.30(5) eV at 6.1 GPa. This collapse is caused by the atomic reorganization after the phase transition, which lead to an enhancement of orbital hybridization. In the HP phase the band gap closes with pressure with pressure coefficient of approximately -15 meV/GPa. This is a consequence of the enhancement of orbital hybridization as pressure increases.

![Figure 11: Pressure dependence of the band-gap energy. Black symbols correspond to compression experiments and white symbols to decompression experiments.](image)

To conclude we will present the results of resistivity measurements, which are shown in Fig. 12. As can be seen in the figure, the resistivity slightly decreases with pressure in the low-pressure phase. PrVO₄ is known to be a high resistivity material, as we found, with electron conduction being mediated by hopping between f-electrons. These electrons are known to gradually delocalize under compression leading thus to the observed decrease of resistivity.
Between 5.3 and 6 GPa we observed a one order of magnitude decrease of the resistivity. This is consistent with the occurrence of the zircon-monazite transition and the related collapse of the band gap. Up to the maximum pressure of the experiments (determined by the used set-up) we observed a gradual change of the resistivity with pressure without any indication of the second phase transition. Under pressure decrease the transition is not reversible, as found in XRD and optical experiments. The large decrease of the resistivity at the phase transition can have a twofold origin: the decrease of the band gap detected by absorption experiments and the formation of imperfections and defects generated during the first-order phase transition from zircon to monazite structure; after the phase transition the latter ones could behave as donor states.\textsuperscript{43,44} It is important to highlight here that no evidence of pressure-induced metallization has been found both in optical and resistivity studies.

\textbf{Figure 12:} resistivity of PrVO\textsubscript{4} versus pressure. Black symbols correspond to compression and white symbols to decompression.

\textbf{Summary}

We have performed a study of PrVO\textsubscript{4} orthovanadate under high-pressure conditions by means of synchrotron powder x-ray diffraction, optical-absorption, and resistivity
measurements. We confirmed that PrVO$_4$ undergoes a first-order transition around 6.2 GPa to a monoclinic monazite-type structure, with a volume collapse of about 9.6%. Further, a second transition to a monoclinic BaWO$_4$-II structure is found around 14.5 GPa, again with a sharp decrease in the volume. Nonetheless, the monazite phase is recovered upon pressure releases. We suggest that the BaWO$_4$-II structure can be the monazite phase of other orthovanadates, by comparison with previous results on NdVO$_4$ and LaVO$_4$. The compressibility of the three structures is found to be anisotropic. The EOS of all phases has also been calculated. The bulk modulus of the zircon phase is found to be comparable to that of soft rare-earth vanadates, such as CeVO$_4$, TbVO$_4$, and TmVO$_4$. Finally, the observed phase transition strongly modifies the electronic properties of PrVO$_4$. Both the band-gap energy and resistivity show an abrupt decrease at the first phase transition. Reasons for these phenomena are discussed, being linked to an enhancement of orbital hybridization induced by pressure.

**Associated Content**

The Supporting Information is available free of charge at arXiv.org.

Axial compressibility for the zircon, monazite and BaWO$_4$-II -type phases; powder XRD measurements, details of the data collections, refinement results, and structural data obtained for PrVO$_4$ at different pressures.

**Author Contributions**

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

**Notes**

The authors declare no competing financial interests.

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PrVO$_4$ under High Pressure: Effects on Structural, Optical and Electrical Properties

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Table S1. Comparison of the linear compressibility for the zircon, the monazite and the BaWO$_4$-II phases as obtained by powder XRD. We also report the variation of the $\beta$ angle of the monazite and BaWO$_4$-II phase with compression.

| Compressibility | Zircon | Monazite | BaWO$_4$-II |
|-----------------|--------|----------|-------------|
| $k_a$ (10$^{-3}$ GPa$^{-1}$) | 3.1(1) | 3.6(1) | 1.1(2) |
| $k_b$ (10$^{-3}$ GPa$^{-1}$) | 3.1(1) | 4.3(1) | 1.60(6) |
| $k_c$ (10$^{-3}$ GPa$^{-1}$) | 1.29(8) | 2.4(2) | 1.69(9) |
| $k_\beta$ (10$^{-2}$ deg GPa$^{-1}$) | -- | -7.1(4) | 1.8(1.3) |
**Table S2:** Details of the data collections, refinement results, and structural data as obtained by powder-XRD experiments on PrVO$_4$ for the zircon, the monazite and the BaWO$_4$-II phase. The pressure at which the refinements were performed is indicated in the table. For the monazite phase, the refinement was performed at 0.4 GPa, after pressure release. In the definition of $R$ factors $Y_i^{obs}, Y_i^{calc}$ indicate observed and calculated peak intensity values, respectively; $w_i$ are the weights and $N$ is the number of data points.

| Source     | Zircon PrVO$_4$ | Monazite PrVO$_4$ | BaWO$_4$-II PrVO$_4$ |
|------------|-----------------|-------------------|----------------------|
| Chemical Formula | PrVO$_4$ | PrVO$_4$ | PrVO$_4$ |
| Formula Weight | 255.85 | 255.85 | 255.85 |
| $T$/K       | 298 | 298 | 298 |
| Pressure    | $10^4$ GPa | 0.4 GPa | 14.45 GPa |
| Wavelength/Å | 0.4246 | 0.4246 | 0.4246 |
| Crystal System | tetragonal | monoclinic | monoclinic |
| Space Group | 141 | 14 | 14 |
| $a$/Å       | 7.3625(2) | 6.9930(8) | 11.557(7) |
| $b$/Å       | 7.3625(2) | 7.1796(7) | 6.522(7) |
| $c$/Å       | 6.4614(4) | 6.6311(8) | 6.847(7) |
| $a$/deg    | 90 | 90 | 90 |
| $\beta$/deg | 90 | 104.60(1) | 90.71(1) |
| $\gamma$/deg | 90 | 90 | 90 |
| $V$/Å$^3$   | 350.26(2) | 322.2(8) | 516.1(8) |
| $Z$         | 4 | 4 | 8 |
| d-space range/Å | 6.08-1.29 | 6.08-1.29 | 6.08-1.29 |
| $\chi^2$   | 5.6169 | 2.4458 | 2.9241 |
| $R_p$       | 0.3719 | 0.3325 | 0.2476 |
| $R_{wp}$    | 0.5259 | 0.5200 | 0.4261 |

**Definition of $R$ factors**

- $R_p = \frac{\sum |Y_i^{obs} - Y_i^{calc}|}{\sum Y_i^{obs}}$
- $R_{wp}^2 = \frac{\sum w_i(Y_i^{obs} - Y_i^{calc})^2}{\sum n w_i(Y_i^{obs})^2}$
- $R_{exp}^2 = \frac{N}{\sum n w_i(Y_i^{obs})^2}$
- $\chi^2 = \left(\frac{R_{wp}}{R_{exp}}\right)^2$