



Exploring the high-pressure behaviour of polymorphs of AMO₄ ternary oxides: crystal structure and physical properties

DANIEL ERRANDONEA

Departamento de Física Aplicada-ICMUV, MALTA Consolider Team, Universitat de València, Edificio de Investigación, C/Dr. Moliner 50, 46100 Burjassot, Valencia, Spain
E-mail: daniel.errandonea@uv.es

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Abstract. AMO₄ ternary oxides are materials of fundamental and technological importance exhibiting a large variety of functional properties. Members of this family of compounds have multiple potential applications; for instance, as scintillators, thermophosphors, photocatalysts, and cathodoluminescence materials. Studies under high-pressure conditions are valuable for understanding the physical properties and phase behaviour of AMO₄ oxides. In particular, great progress has been achieved in the last decade towards the understanding of the pressure-effects on the structural, vibrational, and electronic properties of AMO₄ materials. Specifically, novel metastable structures with interesting physical properties have been discovered. In this article, a selection of recent results from high-pressure studies on different AMO₄ oxides will be discussed, paying particular attention to orthovanadates. Remarkable phenomena like band-gap and volume collapses as well as phonon softening will be discussed and correlated with structural changes.

Keywords. High pressure; oxides; phase transitions; crystal structures; vibrational properties; electronic properties.

1. Introduction

Compounds belonging to the AMO₄ family have interesting properties which make them convenient for technological applications. As a matter of fact, many of them are being employed in the industry.¹ One example of these compounds is the orthovanadate group. These materials have applications in green technologies as photocatalysts for degradation of propane (C₃H₈) and hydrogen sulphide (H₂S), and for hydrogen production by means of photocatalytic water splitting.² During the last decade, high-pressure (HP) techniques have played a decisive role in extending the understanding of the physical properties of AMO₄ oxides. Additionally, they have been also used for synthesizing novel metastable polymorphs and for discovering a plethora of interesting phenomena. In particular, in compounds like bismuth phosphate (BiPO₄) the polymorphism is very rich,³ as illustrated in Figure 1, occurring phase transitions at pressures as low as 2.4 GPa. Interestingly, the metastable polymorphs (BiPO₄-I and BiPO₄-II) obtained by hydration

or at high-temperature (HT), rapidly revert to the stable monazite-type polymorph (space group: $P2_1/n$, $Z = 4$) (BiPO₄-III) under compression. Additionally, the BiPO₄-III polymorph stable under ambient conditions transforms successively into denser polymorphs. In contrast, in other compounds, like bismuth antimoniate (BiSbO₄),⁴ due to the existence of layer-type structural arrangements, the ambient-pressure polymorph is extremely stable. In fact, this compound remains in its monoclinic low-pressure phase (space group: $I2/c$, $Z = 4$) up to at least 70 GPa.⁴ Great progress on the knowledge about the HP behaviour of AMO₄ compounds has been recently achieved by combining experiments with computing simulations.^{5,6}

The focus of this article is to concisely discuss the main characteristics of phase transitions induced under compression in AMO₄ oxides (which has been presented and discussed at the ISMC-2018 symposium), emphasizing recent discoveries. In particular, we will put emphasis on the discussion of results obtained from synchrotron X-ray diffraction (XRD) experiments carried out in three different groups of vanadates and related compounds. The information from

*For correspondence

these experiments allows identifying several pressure-induced phase transitions and accurately determining the crystal structure of the new polymorphs. Results from Raman and optical-absorption measurements will be also presented and discussed to comment on the influence of pressure on vibrational and electronic properties. The set of experimental results will be discussed on the framework of density-functional theory calculations. The combination of all these studies has allowed establishing a systematic understanding of the HP behaviour of AMO_4 compounds, improving the knowledge of their physical properties.

2. Results and Discussion

2.1 InVO_4 and related compounds

The ambient-pressure stable polymorph of InVO_4 ($\text{InVO}_4\text{-III}$) has a crystal structure isomorphous to CrVO_4 . This crystal structure is one of the archetypal AMO_4 structure types adopted by different oxide systems, including vanadates, phosphates, chromates, sulphates, and selenates among others.⁷ The CrVO_4 -type structure of $\text{InVO}_4\text{-III}$ is orthorhombic (space group: $Cmcm$, $Z = 4$). The structure is

schematically shown in Figure 2. It is formed by chains of nearly regular edge-sharing octahedral InO_6 groups which are linked together by tetrahedral VO_4 units. Potential applications of InVO_4 include photovoltaic cells, photocatalysis, lithium-ion batteries, and gas sensors.⁸

A synchrotron powder X-ray diffraction (XRD) study of the HP structural behaviour of InVO_4 has been carried out up to 24 GPa.⁸ In the measurements, in addition to Bragg peaks from the sample, the peaks of Cu (used as a pressure calibrant) and the gasket used as a pressure chamber are detected. However, these peaks do not preclude the identification of the crystal structure of the different phases of InVO_4 . At ambient pressure and for pressures below 6.2 GPa no other phase than $\text{InVO}_4\text{-III}$ is detected. The appearance of extra diffraction peaks at 6.2 GPa (denoted by asterisks in Figure 2) is an indication of the onset of a structural phase transition. At 6.2 GPa the low- and high-pressure phases coexist, being the low-pressure phase the dominant one. At 7.2 GPa, there is still phase coexistence, but the dominant phase is the HP phase (also known as $\text{InVO}_4\text{-V}$). At 8.2 GPa only the HP is present. This has allowed the structural solution and the Rietveld refinement of it, being a monoclinic wolframite-type structure (space group: $P2_1/c$, $Z = 2$) assigned.⁸ This structure is shown in Figure 2.

Interestingly, the HP polymorph of InVO_4 has the vanadium atoms in six coordination, being the structure composed of InO_6 and VO_6 octahedral units. The structural

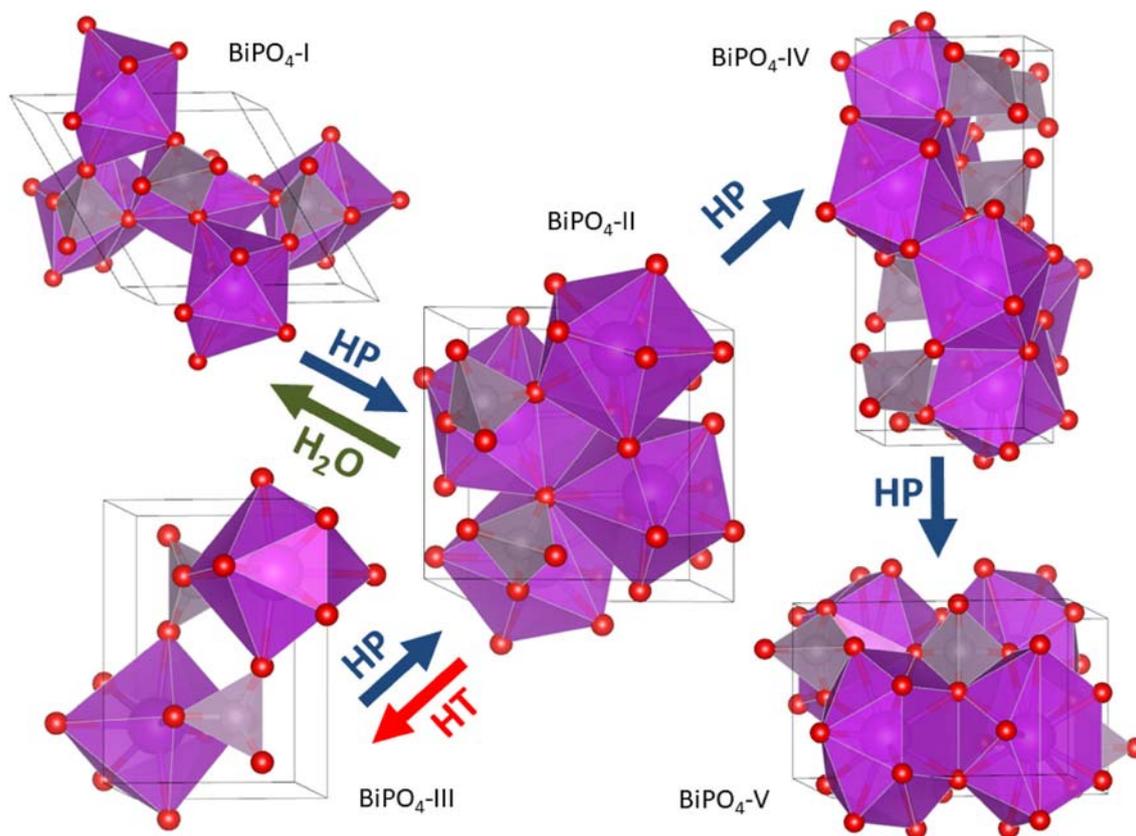


Figure 1. Different polymorphs of BiPO_4 and transformation paths under HT and/or HP, or by water absorption. Arrows indicate the different transitions. PO_4 tetrahedra and the coordination polyhedra of Bi are shown. Notice that phosphorus is in tetrahedral coordination in the five polymorphs.

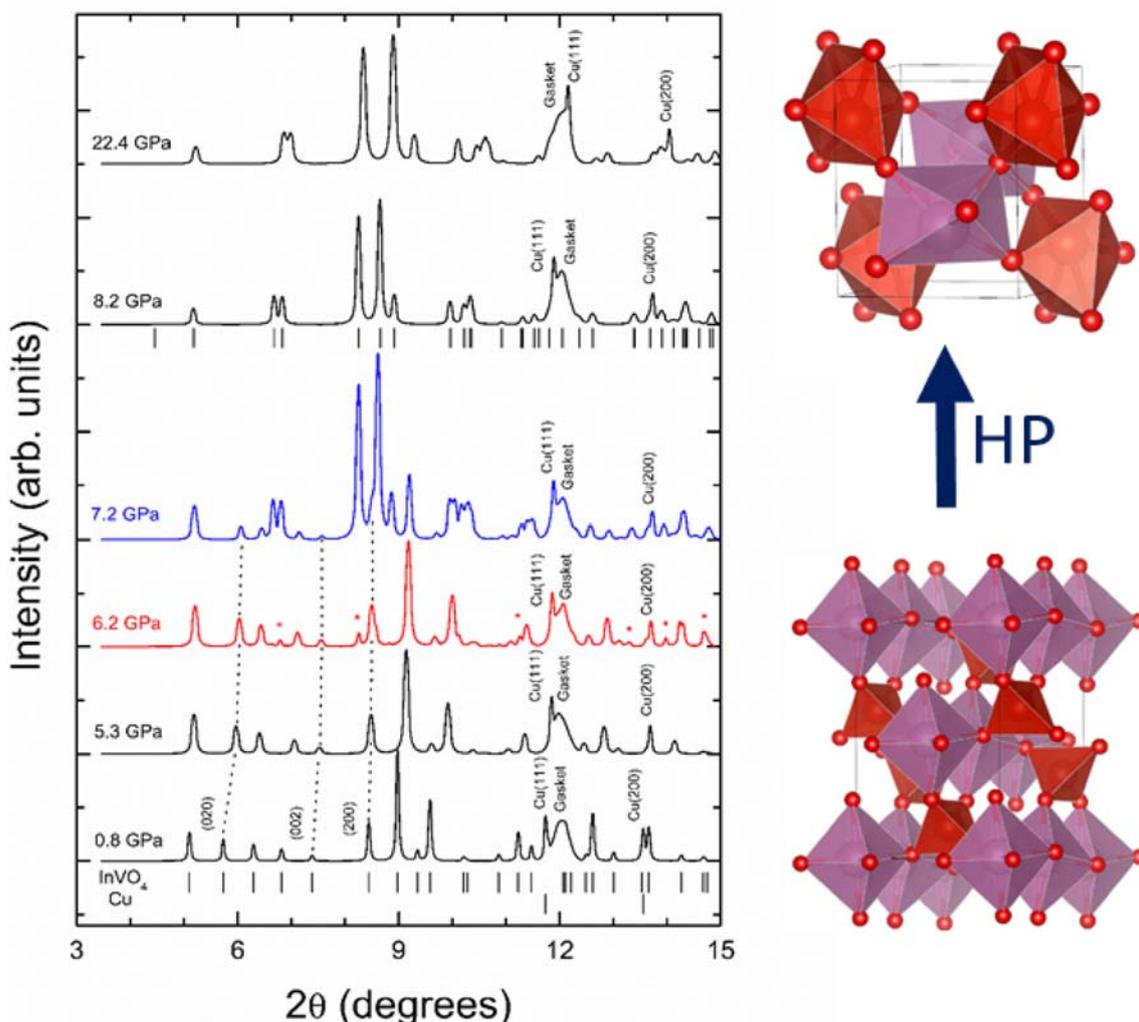


Figure 2. (Left) selection of powder XRD patterns measured under HP conditions using a monochromatic wavelength of 0.4246 Å. Pressures are indicated in the figure. The ticks correspond to the calculated positions for reflections. At 6.2 GPa the asterisks show the peaks of the new phase indicating the onset of the phase transition. At 8.2 GPa the phase transition is completed. (Right bottom) Crystal structure of CrVO₄-type InVO₄. (Right top) Wolframite-type structure of the HP phase of InVO₄. Coordination polyhedra of In (V) are shown in purple (red).

transformation is a first-order transition with a large volume collapse and causes a drastic increase in the bulk modulus.^{8–10} The HP wolframite-type phase remains stable up to 25 GPa.⁸ In addition, both experiments and calculations agree on the fact that the compression of the orthorhombic low-pressure phase is highly anisotropic, being the longest axis, the *b*-axis, the most compressible axis (the reported axial compressibilities are: $\kappa_a = 7.8 \times 10^{-4} \text{ GPa}^{-1}$, $\kappa_b = 8.5 \times 10^{-3} \text{ GPa}^{-1}$, and $\kappa_c = 3.6 \times 10^{-3} \text{ GPa}^{-1}$). The large compressibility of the *b*-axis can be easily understood by assuming an isotropic axial compressibility equal to κ_b . In such a case, the bulk modulus of InVO₄-III would be 39 GPa instead of the measured 69 GPa.⁸ The anisotropic behaviour of the low-pressure phase can be explained by the changes induced by pressure in the InO₆ and VO₄ polyhedral units of CrVO₄-type InVO₄. Basically, the large compressibility of the *b*-axis results from the circumstance that

under compression the InO₆ polyhedra rotates around the *b*-axis. This is caused by the fact that the apical distance of InO₆ is less compressible than the equatorial distance. On the other hand, the presence of incompressible V–O bonds (which are stiffer than the In–O bonds) along the *a*-axis makes it the less compressible axis.

The existence of the reported phase transition is in full agreement with computer simulations performed using density-functional theory (DFT).^{9,10} According to calculations the enthalpy of the HP phase becomes smaller than that of the ambient-pressure phase near 5 GPa,⁹ thus based upon thermodynamic arguments, the phase transition should take place at this pressure. DFT calculations not only helped to understand the observed phase transition but also predicted the existence of additional phase transitions at pressure not yet covered by experiments.⁹ The post-wolframite structure is proposed to be isomorphic with AgMnO₄ (space

group: $P2_1/n$, $Z = 8$).¹¹ This structure is a distortion of the broadly known barite structure (space group: $Pnma$, $Z = 4$). Interestingly, in the case of discovering experimentally, this phase is expected to be formed by InO_8 and VO_8 dodecahedra.⁹ In addition to structural information, the combination of experiments and calculations also gives relevant outputs on the HP behaviour of the electronic band structures, suggesting the existence of band-gap collapse at the $\text{InVO}_4\text{-III}$ -to- $\text{InVO}_4\text{-V}$ phase transition.¹² This conclusion is sustained by resistivity and optical-absorption measurements. Results obtained from them are shown in Figure 3.

In Figure 3, there are several interesting facts that deserve to be discussed. First, in the upper panel it can be seen that the band-gap energy (E_g) is slightly affected by the pressure in the range of stability of the low-pressure phase. In particular, the band-gap slightly blue-shifts under compression. This is a consequence of the fact that the bottom of the conduction band moves in the direction of higher energies faster than the top of valence band. This is caused by the enhancement of the repulsion between bonding and antibonding states of the vanadate ion, which dominates the states near the Fermi level in InVO_4 . Such phenomenon is a result of the decrease of V–O bond-distance under compression.^{8,9} The increase of the band-gap energy has consequences in the electrical resistivity which increases under the application pressure (see the bottom panel of Figure 3). At the transition pressure, there is a collapse of the band-gap energy and an abrupt decrease of the resistivity. The change in the resistivity occurs at a lower pressure than the change in the band-gap energy because resistivity measurements were influenced by non-hydrostatic stresses.¹² The discontinuities in the resistivity and the band gap have been explained by the changes induced by pressure in the crystal structure,¹² which causes drastic changes in the electronic band structure making the band-gap approximately 2.1 eV. They are mainly associated with the increase in the coordination number of V from 4 to 6. The band-gap collapse is correlated to a colour change in InVO_4 , from white transparent to yellowish-orange. The discovered new phase and its electronic properties suggest that (if recovered as a metastable phase), it could be useful for the improvement of green-technology applications; for instance, photocatalytic hydrogen production from water splitting.¹³ For that, it would be important to explore the possibility of obtaining the wolframite-type phase of InVO_4 either as nanoparticle via soft-chemistry methods or as thin films by depositing it in substrates which would induce compression stresses in InVO_4 by the in-plane lattice mismatch.

To complete the picture of the HP behaviour of InVO_4 , a brief comment on lattice vibrations will be included. The orthorhombic low-pressure structure ($\text{InVO}_4\text{-III}$) has the following vibrational representation at the Γ point of the Brillouin zone (BZ): $\Gamma = 5A_g + 4B_{1g} + 6B_{1u} + 3A_u + 2B_{2g} + 7B_{2u} + 4B_{3g} + 5B_{3u}$,⁷ which includes three acoustic ($B_{1u} + B_{2u} + B_{3u}$), three silent (A_u), fifteen Raman-active ($5A_g + 4B_{1g} + 2B_{2g} + 4B_{3g}$), and fifteen infrared(IR)-active ($5B_{1u} + 6B_{2u} + 4B_{3u}$) modes. The

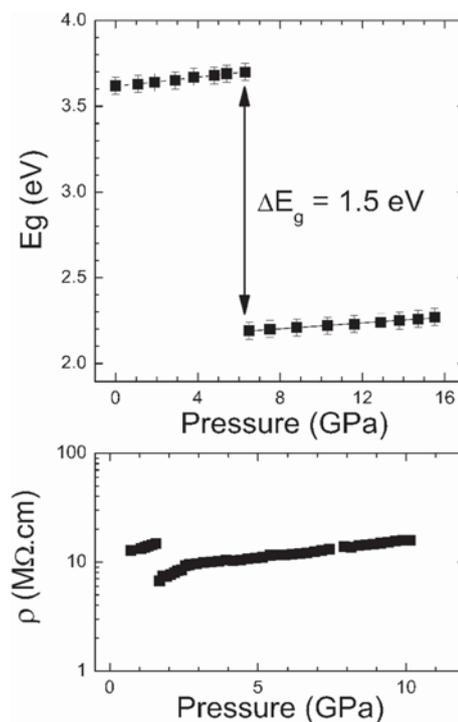


Figure 3. (Top) Pressure dependence of the band-gap energy as obtained from optical-absorption measurements in the near-ultraviolet-visible range (Bottom) Pressure dependence of the resistivity of InVO_4 .

agreement between calculations and experiments regarding Raman and IR frequencies is excellent.⁹ The same can be said for pressure dependences. In particular, the frequencies of the fifteen Raman-active modes of $\text{InVO}_4\text{-III}$ have been accurately determined, being the symmetry of the modes assigned and the mode Grüneisen parameters established.^{8,9} In particular, the high-frequency modes have been correlated to internal vibration of the VO_4 tetrahedron.⁸ A remarkable fact is the presence of one Raman and two infrared modes with negative pressure coefficients. This gradual softening of phonons is believed that could be related to the instability of the crystal structure being one of the possible causes of the observed phase transition.¹⁴ To fully understand the transition mechanism, it would be important to carry out in the future a study of the phonon softening by complimentary techniques like inelastic neutron or X-rays scattering under high pressure.¹⁵

At the phase transition there is a drastic change in the Raman spectrum of InVO_4 .⁸ Among other things the number of phonons is increased and there is a considerable decrease in the frequency of highest frequency Raman mode. This increase in the number of Raman modes is explained by the decrease of the crystal symmetry after the phase transition. The second observation is a consequence of the increase of the coordination number of V. Note that this mode is associated with an internal stretching vibration of the VO_4 (VO_6) polyhedron in $\text{InVO}_4\text{-III}$ ($\text{InVO}_4\text{-V}$). The coordination increase triggered by the transition has

associated and enlargement of the V–O bonds with the consequent decrease of the constant force associated with the stretching vibration, which as expected causes a drop of the corresponding phonon frequency. For the HP phase, group theory predicts the following phonon modes: $\Gamma = 8A_g + 10B_g + 8A_u + 10B_u$, which include three acoustic ($2B_u + 1A_u$), eighteen Raman ($8A_g + 10B_g$), and fifteen infrared ($7A_u + 8B_u$) modes. Raman experiments have been performed up to 16.9 GPa, finding additional evidence of the already described phase transition. On top of that, it has been found that HP InVO_4 -V has various Raman and infrared modes with negative pressure coefficients. Indeed, calculations predict the complete softening of an infrared mode at a pressure slightly smaller than those of the proposed second HP transition.⁹ This observation is suggesting that the transition could be not only thermodynamically driven but also mechanically driven. The detailed study of the phonon softening could be a useful tool to understand the transition mechanism.¹⁶

Conclusions from vanadates can be used to understand the HP behaviour of phosphates. Being isostructural, vanadates could mimic the effects of pressure in phosphates but at lower pressures, making easy their study. Based upon the results described above, it is expected that formation of crystal structures with hexa-coordinated phosphorous (a rare coordination for this element)¹⁷ in CrVO_4 -type phosphates. Theoretical studies support this hypothesis,¹⁸ proposing that wolframite-type InPO_4 and TiPO_4 (with six-coordinated phosphorous) could be obtained at room-temperature (RT) under the application of 50 GPa, a pressure that can be obtained routinely now-a-days in laboratories. The proposed crystal structures have not been found so far; however, it has been recently reported than in TiPO_4 , a sequence of structural transformation leads to HP TiPO_4 -V (space group: $P2_1/c$, $Z = 4$),¹⁹ which is stable beyond 46 GPa. In this structure phosphorous has an infrequent oxygen five coordination. HP TiPO_4 -V remains stable up to 56 GPa. The discovery of this polymorph has triggered new findings like the formation of a post-coesite form in phosphorus oxonitride at 17 GPa.²⁰ In this structure, a 5+1 octahedral coordination is formed for P; indicating that the formation of a six-fold coordination of phosphorous in phosphates might be plausible at RT and relatively low pressures.

Crystal-chemistry is an effective instrument to qualitatively understand and make predictions on the HP behaviour of AMO_4 oxides. In particular, the diagram developed by Bastide²¹ has been proven to be a useful tool for understanding HP structural sequences and predicting phase transitions.^{5,6} According to these ideas, pressure-induced transitions would probably occur from the stable structure of a given compound to that of a larger-cation-hosting material with a similar stoichiometry. An example of it is the well-known HP transition from zircon (ZrSiO_4) to scheelite (CaWO_4). Following this understanding, compounds like InTaO_4 and InNbO_4 , which crystallize in the wolframite-type structure (isomorphic to the HP crystal structure of InVO_4), can be a good model in order to try to

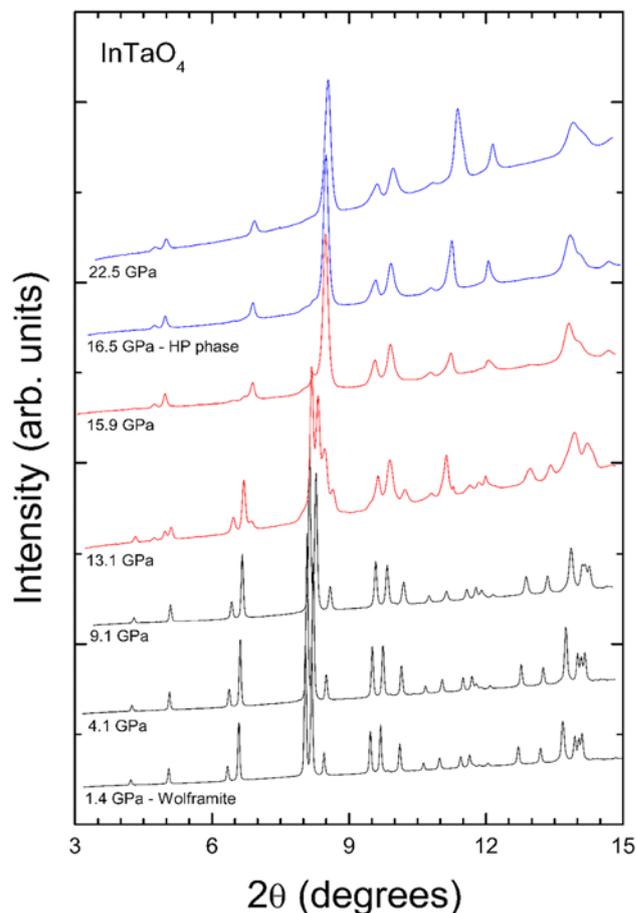


Figure 4. XRD patterns measured in InTaO_4 at selected pressures ($\lambda = 0.4246 \text{ \AA}$). We show in black the patterns assigned to the low-pressure phase, in red those corresponding to phase coexistence, and in blue those assigned to the HP phase.

get information on possible post-wolframite transitions in compounds like InVO_4 and InPO_4 . InTaO_4 and InNbO_4 have been studied up to 23 GPa.^{22,23} In both compounds a phase transition induced by pressure has been discovered.

Figure 4 shows a selection of powder XRD patterns measured under HP in InTaO_4 . The low-pressure wolframite-type structure remains stable up to a pressure close to 13 GPa. At 13.1 GPa the appearance of new diffraction peaks is detected.²² This corresponds to the onset of a structural phase transition. The peaks of the HP phase gradually gain in intensity as pressure increases while those of the low-pressure phase become weaker. The phase coexistence region extends from 13.1 to 15.9 GPa (as can be seen in the XRD patterns shown in red in the figure). At 16.5 GPa only the HP is detected, remaining stable up to the highest pressure covered by the experiments.

The HP phase has been assigned to a monoclinic structure described by the same space group than wolframite ($P2_1/c$).²² However, the transition is first-order, involving a contraction of the volume collapse of 10% and an increase in the coordination of both cations from six to eight. The HP

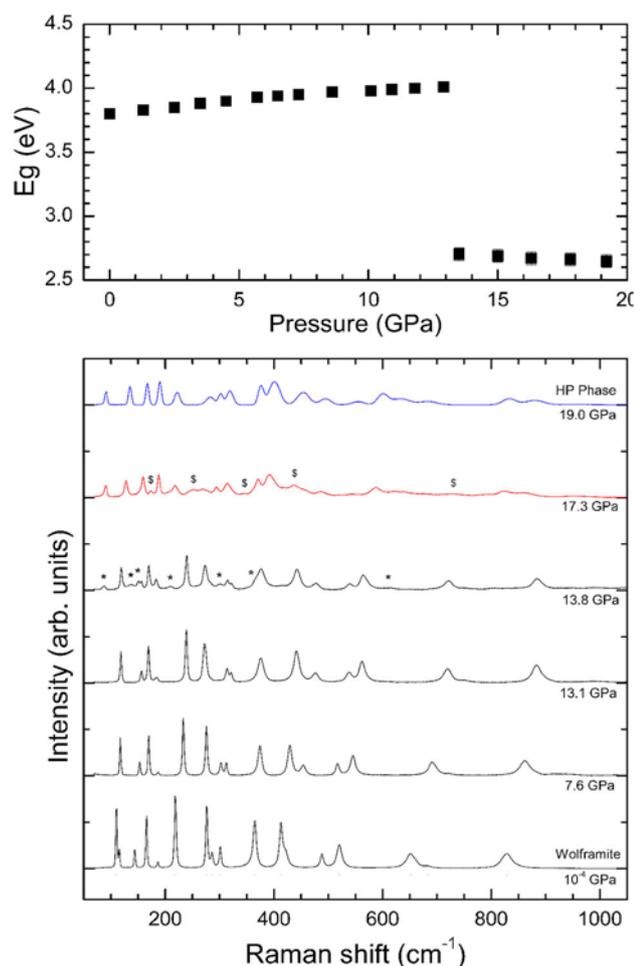


Figure 5. (Top) pressure dependence of the band-gap energy of InTaO₄. (Bottom) Raman spectra of InTaO₄ at selected pressures. Asterisks denote the appearance of Raman modes of the HP phase and dollar symbols weak peaks of the low-pressure phase detectable at 17.3 GPa.

structural sequence of InNbO₄²³ is analogous to that of InTaO₄. These results invite for the searching of post-wolframite structures in InVO₄ in which V is eight coordinated by oxygen atoms.

The conclusions obtained from XRD experiments have been confirmed by *ab-initio* calculations, Raman spectroscopy studies, and optical-absorption measurements in InTaO₄ and InNbO₄.^{12,22,23} To illustrate it, in Figure 5 a selection of Raman spectra is shown. Up to 13.1 GPa there are no qualitative changes in the Raman spectra, mainly most modes harden under compression and some of them merge because of their different pressure dependences. However, several new Raman modes (shown with asterisks) can be seen at 13.8 GPa, confirming the onset of the phase transition found in XRD experiments.

As in XRD experiments, in Raman measurements, there is a pressure range of phase coexistence. Indeed, weak modes of the low-pressure phase (indicated by dollar symbols) can be traced up to 17.3 GPa. The Raman

spectrum of a pure HP phase can be seen at 19.0 GPa. The HP phase of InTaO₄ and InNbO₄ has eighteen Raman-active modes. Their frequencies and pressure dependences have been accurately determined.^{22,23} The increase of the number of modes in the high-frequency region, which are internal vibrations of the Ta (or Nb) coordination polyhedron, and the drop of the frequency of the highest frequency mode is connected with the increase of the coordination number of the pentavalent cation.

From the optical-absorption experiments the pressure dependence of the band-gap energy (E_g) has been obtained. From the measurements it has been concluded that InNbO₄ and InTaO₄ are wide band-gap materials with $E_g > 3.6$ eV (in the near ultraviolet). In the low-pressure phase the band-gap slightly blue shifts (see Figure 5) as a consequence of the increase of the splitting between bonding and antibonding states of the tantalate (niobate) ion.^{24,25} On the other hand, the structural changes caused by the phase transition trigger a collapse of the band gap to values close to 2.5 eV. This phenomenon is a consequence of the increase of the orbital hybridization, which is related to the decrease of bond distances and the increase of the coordination number of Ta (Nb) at the phase transition.

Before closing this section, a comment will be added about compounds which has been little studied but in which HP could lead to interesting results according to the results summarized above. One of them is FeVO₄, which is polymorphic, being one of the polymorphs isostructural with InVO₄-III. It is known that in this compound, a wolframite-type phase can be obtained upon the joint application of pressure and temperature.²⁶ However, its phase diagram is much more complicated than in InVO₄, mainly due to the magnetic interaction between Fe atoms. In particular, three different phase transitions have been predicted by calculations and found by XRD measurements for pressures smaller than 12 GPa.²⁷ One of the HP phases is isomorphic with wolframite (FeVO₄-IV) and has been found around 6 GPa. FePO₄ is another interesting compound which has been little studied under compression. In this compound the CrVO₄-type polymorph can be obtained at 0.5 GPa and 900 °C.²⁸ However, it has never been studied under compression. Indeed, only the berlinite-type polymorph (space group: $P3_121$, $Z = 3$) has been studied under HP. It has been reported that pressure drives the low-pressure phase into two coexisting antiferromagnetic states; one amorphous designated as FePO₄-IIb and the other crystalline and isostructural to CrVO₄, which has been named as FePO₄-IIa.²⁹ In these phases the Neel temperature increases under compression. Another interesting case for future studies is the metastable HP CrVO₄-type variety of GaAsO₄³⁰ and MgSO₄.³¹ The last compound has been recently studied using DFT calculations. Several HP phase transitions have been proposed, but in contrast with other cations, sulfur is believed to retain the tetrahedral coordination in all the proposed HP polymorphs.

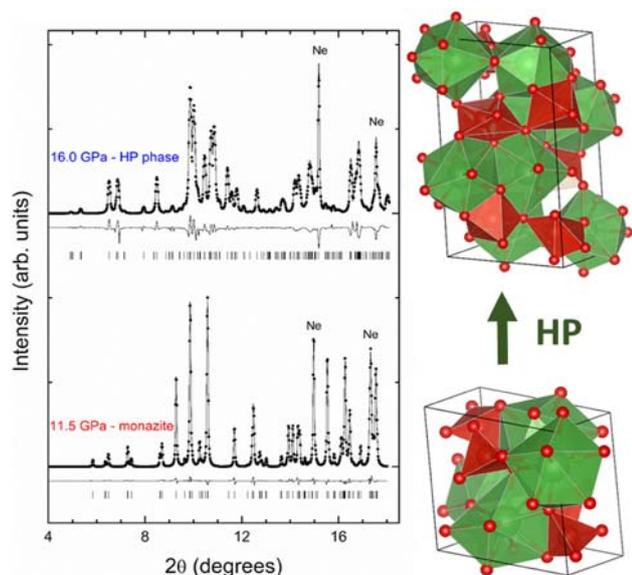


Figure 6. (Left) Powder XRD patterns measured in LaVO_4 at 11.5 GPa (low-pressure phase) and 16.0 GPa (HP phase); $\lambda = 0.534$ Å. Experiments (dots), refinements, and residuals are shown. Ticks show the position of the reflexions. Ne indicates the Bragg peaks of the pressure medium which solidifies at 4 GPa. (Right) Schematic view of the LP (bottom) and HP phase (top). Coordination polyhedra of La (V) are shown in green (red).

2.2 LaVO_4 and related compounds

LaVO_4 is the only member of the orthovanadate family which adopts the monazite-type structure (space group: $P2_1/n$, $Z = 4$).³² This structure is shown in Figure 6. On it, V and La are four- and nine-fold coordinated, respectively. The crystal structure of monazite is common to a large number of AMO_4 oxides including phosphates, chromates, selenates, etc.³³ These compounds have been the focus of attention of HP studies.³⁴ Results from HP XRD studies on LaVO_4 are shown in Figure 6. This compound has been studied by different authors up to 30 GPa.^{35–38} The most relevant result is the existence of a phase transition when LaVO_4 is squeezed up to 12 GPa at room temperature. The transition pressure depends on the conditions of the experiments, being reduced by more than 3 GPa if conditions are not hydrostatic.

The occurrence of the phase transition can be seen in Figure 6 by comparing the two powder XRD patterns. The experiments were performed using neon (Ne) as pressure medium to guarantee quasi-hydrostatic conditions. The XRD pattern at 11.5 GPa was successfully indexed and Rietveld refined assuming the monazite structure, supporting that this polymorph is stable up to this pressure. The XRD pattern at 16.0 GPa is qualitatively different. There are noticeable changes. In particular, there are Bragg peaks appearing at low angles, which suggest a larger unit cell than in monazite. The structure of the HP phase has been solved, being assigned to a monoclinic structure described

by the same space group that monazite ($P2_1/n$), but having eight formula units per unit cell ($Z = 8$).³⁸ The HP structure of LaVO_4 is shown in Figure 6. It is isostructural to the BaWO_4 -II-type structure common in tungstates.

The occurrence of the reported phase transition has been confirmed by Raman spectroscopy and *ab-initio* calculations.³⁸ The combination of the three techniques has allowed characterizing precisely the pressure evolution of unit-cell parameters and the Raman and infrared of the low- and high-pressure polymorphs of LaVO_4 . The increase of the size of the unit-cell at the phase transition causes substantial changes in the Raman spectrum, increasing the number of Raman-active modes from 36 to 72. At the phase transition, there is a considerable decrease in the volume. This and the atomic reorganization indicate a first-order phase transition. In particular, the phase transition implies an increase of the coordination number of V from four to six and of the coordination number of La from nine to ten. It should be not a mere coincidence of the fact that V coordination is increased by pressure in monazite-type and CrVO_4 -type compounds.

In order to investigate the changes caused in the electronic properties by pressure-driven structural changes, optical-absorption and luminescence measurements have been carried out in pure and Nd^{3+} -doped LaVO_4 crystals up to 25 GPa.³⁹ These experiments have been interpreted with the help of band-structure and crystal-field calculations.³⁹ It has been found that both optical-absorption and luminescence measurements evidence that a phase transition takes place close to 12 GPa, in agreement with XRD and Raman studies.³⁸ The information obtained on the pressure dependence of the band-gap is shown in Figure 7. Radical changes take place in the optical properties of LaVO_4 when the phase transition from monazite to BaWO_4 -II occurs. In particular, there is a contraction of the band gap of nearly 0.6 eV. It causes a noticeable colour change in LaVO_4 as

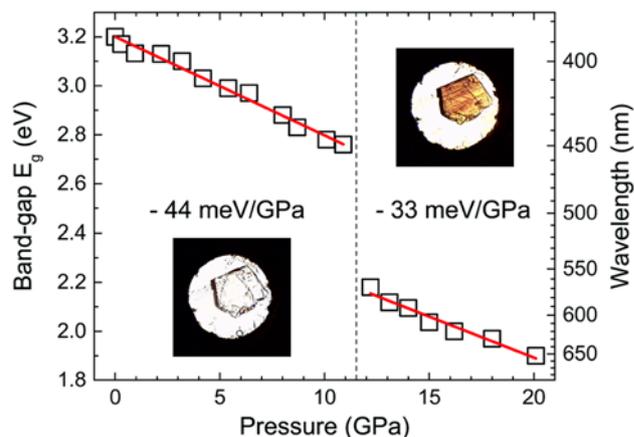


Figure 7. Pressure dependence of the band-gap energy of LaVO_4 (given in eV on the left and in nm on the right). Within the figure pictures taken in the low- and high-pressure phases are shown to illustrate the colour change caused by the band-gap collapse.

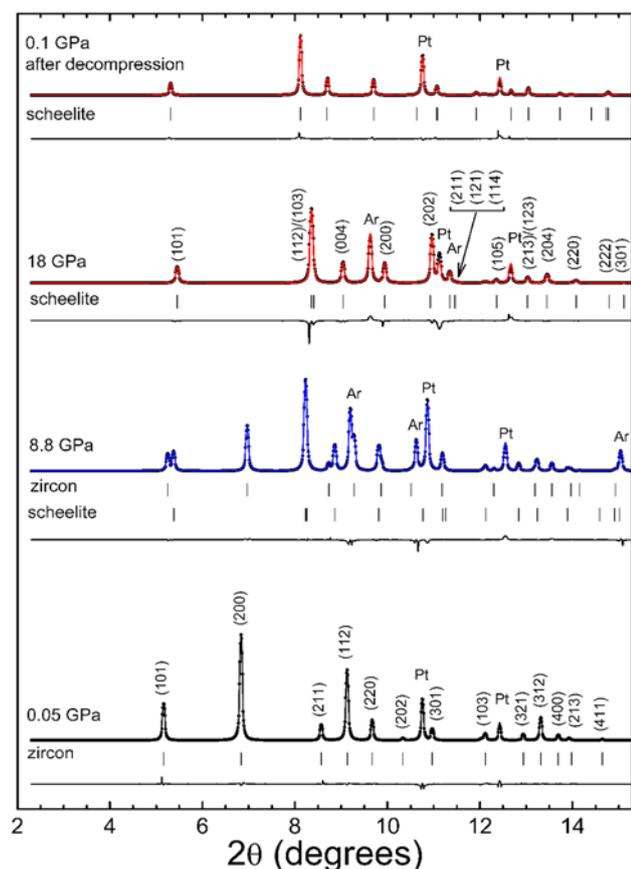


Figure 8. XRD patterns measured in HoVO_4 at different pressures. The experiments were carried out using argon as pressure medium and with a wavelength of 0.4246 Å. Patterns from different phases have been Rietveld refined. Experimental results, refinements, and residuals are shown. The ticks indicate the position of Bragg peaks. The indexes of the peaks from zircon (low-pressure phase) or scheelite (high-pressure phase) are given. Pt and Ar denote peaks from platinum (pressure calibrant) and argon (pressure medium).

shown in Figure 7. The changes have been correlated to the modification of the coordination number of vanadium. Interestingly in both phases the band gap red-shifts with pressure (pressure coefficients are given in the figure). This result is in contrast with results obtained from zircon-type and CrVO_4 -type orthovanadates^{12,24} in which the band-gap slightly blue-shifts under compression. This distinctive behaviour of LaVO_4 is due to the non-negligible contribution of La 4f and 5d states to the bottom of the conduction band.³⁹

The existence of pressure-induced phase transitions on monazite-type phosphates has been broadly studied during the last few years.^{3,40–45} In addition, the influence of pressure on the structural, vibrational, and elastic properties have been studied too.^{41–44} The obtained results are particularly relevant for geochronology of shear zones in the Earth mantle.⁴⁶ All the studied phosphates have been found to remain in the monazite structure up to nearly 30 GPa.

The lowest transition pressure has been observed in LaPO_4 (~ 26 GPa). The structure of the post-monazite phase has been obtained from single-crystal XRD experiments corresponding to a post-barite-type structure with space group $P2_12_12_1$ ($Z = 4$).⁴⁵ In the case of BiPO_4 , the phase transition was experimentally found at 28 GPa after the synchronised application of pressure and temperature (1500 K).³ For the HP polymorph of BiPO_4 , the crystal structure has been assigned to a scheelite-type structure (space group: $I4_1/a$, $Z = 4$). The existence of both transitions is in full agreement with the crystal-chemistry arguments used to discuss the results summarized in the previous section.³⁴ They are also consistent with results from *ab-initio* simulations.^{47,48} Calculations have predicted the existence of a post-scheelite structure in BiPO_4 , forecasted to occur at 52 GPa, having the new polymorph a barite-type structure, related to the HP form of LaPO_4 .³ In spite of the progress done on the study of monazite-type phosphates, very little has been performed on solid solutions of these compounds, like those recently carried out for $(\text{Sm},\text{Tb})\text{PO}_4$ mixtures, which crystallize in different structures depending on the Tb content.⁴⁹ The study of these solutions can be quite useful to deepen the understanding of the HP behaviour of monazite-type phosphates. Other issues of interest to be explored in the future are the solubility of monazite phosphates in aqueous solutions upon compression⁵⁰ and the behaviour of radiation-damaged monazites⁵¹ under HP.

The third group of monazite-type oxides which has been studied under HP is chromates. For instance, SrCrO_4 has been found to undergo a monazite–scheelite transition near 10 GPa and a second transition to a AgMnO_4 -type structure, a distortion of barite near 13 GPa.⁵² Extension of the pressure range up to 58 GPa gives undoubtedly evidence of two additional phase transitions at 35 and 48 GPa.⁵³ These transitions drive numerous changes in the vibrational and electronic properties with the new high-pressure phases having a low conductivity. Unfortunately, the crystal structure of these phases has not been determined yet. On the other hand, no indication of chemical decomposition or metallization of SrCrO_4 was detected up to 58 GPa. In the case of PbCrO_4 , it has been found that phase transitions can be very sensitive to stresses between grains. In particular, powder and single-crystal XRD experiments lead to a slightly different HP structural sequence.^{54–56} However, all experiments and calculations agree on the fact that scheelite is one of the HP phases of PbCrO_4 (like in SrCrO_4). The post-scheelite structure has been proposed to be a distortion of barite, resembling the HP polymorphs found in other monazites. HP resistivity, Hall-effect, and optical-absorption measurements in PbCrO_4 ⁵⁷ have shown that the structural changes transform the compound from a wide-band-gap semiconductor to a narrow-band-gap semiconductor, changing the band-gap energy from 2.3 eV at ambient pressure to 0.8 eV at 20 GPa.

A final case that deserves to be commented is anhydrite CaSO_4 , which is known to transform under compression subsequently into monazite and AgMnO_4 -type.⁵⁸ In this

compound, the simultaneous application of pressure and temperature (1450 K) leads to the transformation into the barite-type structure,⁵⁸ suggesting that the HP behaviour of monazite could be influenced by the presence of kinetics barriers. A similar HP behaviour has been theoretically predicted for CaSeO_4 .⁵⁹ For this compound two transitions to scheelite and AgMnO_4 -type have been predicted. However, these predictions are awaiting to be confirmed since AsSeO_4 selenates have not been experimentally studied under HP so far.

2.3 Zircon-type compounds

Most of the rare-earth orthovanadates crystallize in a tetragonal zircon-type structure (space group: $I4_1/amd$, $Z = 4$).^{60,61} This structure is also shared by YVO_4 , ScVO_4 , and BiVO_4 . Zircon is a prototypic structure also shared by silicates and phosphates among other oxides. In the case of AVO_4 vanadates, the structure is composed of chains of VO_4 tetrahedral units and AO_8 dodecahedral units. It can be also seen as a superstructure of the XO_2 rutile (space group: $P4_2/mmm$, $Z = 2$) structure of dioxides, in which the alternate substitution of X atoms by A and V atoms doubles the size of the unit-cell. Since the beginning of the 21st century, this family of vanadates has been extensively studied under HP.⁶ After the work by Wang *et al.* in YVO_4 , in which a zircon–scheelite transition was discovered around 8.5 GPa,⁶² and equivalent transition was found in many other zircon-type vanadates.^{63–74} The transition has been broadly discussed in the literature. It does not involve any change in the coordination sphere of the cations. Indeed, the VO_4 tetrahedron is basically not modified after the transition. However, the transition implies a large volume collapse and a reorientation of the different polyhedra to increase the packing efficiency (and consequently the density) of the material. The transition is irreversible and first order. Consequently, on pressure release, the HP phase is retained as a metastable phase. The zircon–scheelite transition has been reported for ScVO_4 and rare-earth vanadates going from SmVO_4 to LuVO_4 . The main effect on the physical properties is the enhancement of the bulk modulus and a large collapse of the electronic band-gap, which has been extensively discussed by Panchal *et al.*²⁴ As a first approximation the band-gap collapse is caused by the reasons described in the previous section for the abrupt decrease of the band-gap observed in LaVO_4 .

In order to illustrate the occurrence of the zircon–scheelite transition in vanadates, in Figure 8 we show a selection of XRD patterns measured in HoVO_4 at different pressures. The experiments were performed under quasi-hydrostatic conditions, being argon (Ar) the pressure medium. The quality of the XRD patterns allow for Rietveld refinements of the crystal structure of the HP phase as shown in the figure. Notice that there is a pressure region where both the zircon and scheelite phases coexist. For instance, in the XRD pattern at 8.8 GPa in Figure 8. In the

figure it can be also seen that the HP scheelite-type polymorph remains stable upon decompression.

The study on HoVO_4 leads to important conclusions which have been generalized for many compounds of the family. One is that the transition pressure is highly influenced by the presence of non-hydrostatic stresses. In particular, in HoVO_4 the transition pressure can be lowered from 8.2 GPa to 4.5 GPa. The other conclusion is the existence of a second phase transition beyond 20.4 GPa from scheelite to fergusonite (space group: $I2/a$, $Z = 4$) a monoclinic distortion of it. The third conclusion is that large exposition of vanadates to X-rays under HP can lead to partial decomposition of the ternary oxides into their constituent binary oxides. This phenomenon is apparently induced by photoelectric processes.⁷² The influence of non-hydrostaticity in the results can be so important, that in the case of ScVO_4 , in experiments done under highly non-hydrostatic conditions, a direct transition from zircon to fergusonite has been found.⁷³

Another conclusion about which most authors agree is the fact that vanadates with rare-earths with a large radius (namely NdVO_4 , PrVO_4 , and CeVO_4) instead of transforming under compression into the scheelite structure prefer to transform into monazite, the structure of LaVO_4 .^{6,68} However, it has been shown recently that non-hydrostaticity could influence the structural sequence. In particular, in the case of NdVO_4 ⁷⁴ it has been found that when experiments are performed using methanol–ethanol–water as the pressure medium the zircon–monazite transition is observed, but when experiments are carried out using helium as pressure medium (the medium where non-hydrostaticity is minimized),⁷⁵ the transition is from zircon to scheelite. This highlights the relevance of non-hydrostatic stresses, which should be systematically studied in the future.

The goal of future studies should be also the systematic determination of post-scheelite and post-monazite structures, which has been accurately determined only for a few compounds.⁶ Another interesting issue is the study of a possible induced amorphization as well as pressure-induced metallization, which has been predicted to occur at relative low pressure by a process of charge transfer and band overlaps,⁷⁶ but has not been observed so far, even in studies up to 50 GPa. A third issue to be explored in the future is combined HP and high-temperature experiments, like those recently performed in ErVO_4 .⁷⁷ This study showed that at ambient pressure the zircon phase transforms into scheelite around 800 K, decreasing the transition temperature as pressure increases, taking place the phase transition at 300 K at 8.2 GPa. Since the volume of scheelite is smaller than that of zircon, a phase boundary with a negative slope can be only possible if the entropy of scheelite is higher than that of zircon, according to the Clausius–Clapeyron relation. ErVO_4 is the only compound where such studies have been carried out. Similar studies in related vanadates will be helpful to better understand the mechanism of the zircon–scheelite transition.

To conclude we would like to state that the results here discussed are relevant not only for vanadates but also for phosphates, germanates, and silicates,^{40,78–80} for which the zircon–scheelite and zircon–monazite transitions take place at higher pressures. Therefore, vanadates can be used to mimic their HP behaviour. The existence of a second transition in vanadates at relative low pressure (smaller than the pressure of the first transition in silicates and phosphates) gives the possibility of discoveries which can open new avenues for the study of the HP behaviour of phosphates and silicates isomorphous to vanadates.

3. Conclusions

A comparison of the HP behaviour of different AMO_4 oxides has been presented. In particular, conclusions from recent HP studies have been summarized including results from XRD, Raman, and optical measurements, as well as density-functional theory calculations. InVO_4 , LaVO_4 , HoVO_4 , and isostructural compounds have been used as examples to illustrate the current understanding of the HP behaviour of AMO_4 oxides. A systematic interpretation of the experimental evidence is proposed. In addition, the relation of phase transitions with phonon properties and electronic properties has been discussed. The reviewed studies provide relevant information for the development of technological applications of ternary oxides.

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