Zircon to monazite phase transition in CeVO$_4$: X-ray diffraction and Raman-scattering measurements


$^1$Departamento de Física Aplicada-ICMUV, MALTA Consolider Team, Universidad de Valencia, Edificio de Investigación, C/Dr. Moliner 50, 46100 Burjassot (Valencia), Spain

$^2$Departamento de Física Fundamental II, Instituto de Materiales y Nanotecnología, Universidad de La Laguna, La Laguna 38205, Tenerife, Spain

$^3$Departamento de Química Física – MALTA Consolider Team, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

$^4$Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain

$^5$Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

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X-ray diffraction and Raman-scattering measurements on cerium vanadate have been performed up to 12 and 16 GPa, respectively. Experiments reveal at 5.3 GPa the onset of a pressure-induced irreversible phase transition from the zircon to the monazite structure. Beyond this pressure, diffraction peaks and Raman-active modes of the monazite phase are measured. The zircon-to-monazite transition in CeVO$_4$ is distinctive among the other rare-earth orthovanadates. We also observed softening of external translational $T(E_u)$ and internal $v_2(B_{2g})$ bending modes. We attribute it to mechanical instabilities of zircon phase against the pressure-induced distortion. We additionally report lattice-dynamical and total-energy calculations which are in agreement with the experimental results. Finally, the effect of nonhydrostatic stresses on the structural sequence is studied and the equations of state of different phases are reported.

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I. INTRODUCTION

Recently significant research has been carried out in the field of zircon-type orthovanadates (AVO$_4$, $A =$ trivalent atom) due to their wide practical applications. Orthovanadates are well known for birefringent materials and optical polarizers. These materials are potential candidates for laser-host materials and also find applications in other fields such as cathodoluminescent, thermophosphors, scintillators, phosphors, and nuclear-waste storage materials.$^{1–3}$ In general, the AVO$_4$ orthovanadates crystallize in two polymorphs, a tetragonal zircon-type structure$^4$ [space group (SG): $I4_1/amd$] and a monoclinic monazite type$^5$ (SG: $P2_1/n$). The zircon structure is composed of alternating edge-sharing AO$_6$ dodecahedra and VO$_4$ tetrahedra forming chains parallel to the $c$ axis, while in the monazite structure AO$_9$ polyhedra are edge shared with VO$_4$ tetrahedra along the $c$ axis (see Fig. 1).

The phase stability of lanthanide-based ABO$_4$ compounds depends on the $A/B$ cation size ratio, and those with a large ionic radius, like LaVO$_4$, crystallize in the monazite structure. The compound CeVO$_4$, with Ce having a smaller ionic radius than La, crystallizes in the zircon structure, although it is located close to the boundary of the zircon and monazite structures. Hence, the zircon phase is expected to undergo a structural phase transition at a relatively low pressure compared with that of other orthovanadates. In view of the nature of the structural phase transitions in these compounds, it is quite imperative to understand the behavior of the zircon-structured orthovanadates under hydrostatic compression and verify whether the cation $A$ radius plays any vital role in the structural phase transitions. As a matter of fact, most of the rare-earth orthovanadates have been observed to undergo an irreversible zircon-to-scheelite phase transition.$^6$ However, rare-earth-based zircon compounds with relatively large ionic radii, like CeVO$_4$, NdVO$_4$, and PrVO$_4$, have not been investigated so far.

Recent high-pressure (HP) measurements performed in orthophosphates evidence the importance of the cation $A$ ionic radius in the sequence of structural phase transitions. Raman spectroscopy measurements and lattice-dynamic calculations supported by x-ray diffraction (XRD) in TbPO$_4$ indicate a zircon-to-monoclinic phase transition at 9.5 GPa.$^7,8$ Similarly an XRD investigation in orthophosphates, viz. YPO$_4$ and ErPO$_4$, reports a zircon-to-monazite phase transition in both compounds.$^9$ On the other hand, ScPO$_4$, YbPO$_4$ and LuPO$_4$ undergo a reversible zircon-to-scheelite phase transition.$^{10,11}$ Thus it is a key issue to find what factor governs both zircon-to-scheelite and zircon-to-monazite phase transitions in orthovanadates and orthophosphates. In this paper we report XRD and Raman scattering measurements in CeVO$_4$, the mineral wakefieldite (Ce), up to 12.0 and 15.9 GPa, respectively, together with ab initio calculations.

II. EXPERIMENTAL DETAILS

CeVO$_4$ samples were prepared by a solid-state reaction of appropriate amounts of predried Ce$_2$O$_3$ (Indian Rare Earth Ltd., 99%) and V$_2$O$_5$ (Alfa-Aesar, 99%). Homogeneous mixtures of the reactants were pelletized and heated at 800 °C for 24 h and then cooled to ambient temperature. Further, the pellets were reground and heated again at 1100 °C for 24 h. The sample obtained was characterized by XRD as a single phase of CeVO$_4$ of a zircon-type structure.
Angle-dispersive powder XRD measurements both at ambient pressure and at HP were recorded on the 135-mm Atlas change-coupled device (CCD) detector placed at 110 mm from the sample of an Xcalibur diffractometer (Oxford Diffraction Limited) using \( K_{\alpha 1}:K_{\alpha 2} \) molybdenum radiation. The x-ray beam was collimated to a diameter of 300 \( \mu m \). The same setup was used previously to successfully characterize the HP phases in ABO\(_4\) oxides up to 20 GPa.\(^{12}\) On the other hand, Raman measurements both at ambient pressure and HP were performed in the backscattering geometry using a 632.8-nm He–Ne laser and a Horiba Jobin–Yvon LabRAM high-resolution microspectrometer in combination with a thermoelectric-cooled multichannel CCD detector with spectral resolution below 2 cm\(^{-1}\).

For HP measurements on CeVO\(_4\), a finely grounded powder sample of CeVO\(_4\), along with 2-\( \mu m \)-diameter ruby balls, was loaded in a preindented steel gasket with a 200-\( \mu m \)-diameter hole inside a diamond-anvil cell (DAC). A 4:1 methanol-ethanol mixture was used as the pressure-transmitting medium.\(^{13,14}\) The pressure was determined using the ruby-fluorescence technique.\(^{15}\) A modified Merrill–Bassett DAC was used for XRD measurements and a membrane-type DAC was used for Raman measurements.

We also performed compression measurements in CeVO\(_4\) at ambient and high temperatures using steel-belted Bridgman-type opposed tungsten-carbide anvils with a tip 15 mm in diameter.\(^{16}\) The sample was contained in a pyrophylite chamber which consists of two pyrophylite gaskets of optimized thickness (0.5 mm each) in a split gasket geometry. Cubic boron nitride was the pressure medium used in these experiments. To increase the temperature we used a graphite heater.\(^{17}\) Temperature was measured using a steel-shielded K-type thermocouple and pressure by the calibration of the load applied to the anvils against HP resistivity transitions in Bi, Yb, CdTe, and \( n \)-type InSe.\(^{18}\) Effects of pressure in the thermocouple were neglected. Recovered samples from different experimental runs were analyzed by XRD and Raman spectroscopy.

### III. THEORETICAL METHOD AND COMPUTATIONAL DETAILS

It is well known that \textit{ab initio} methods have allowed detailed studies of the energetics of materials under HPs.\(^{19}\) Total-energy calculations were done within the framework of the density-functional theory (DFT), and the Kohn–Sham equations were solved using the projector-augmented wave (PAW)\(^{20,21}\) method as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^{22}\) We used a plane-wave energy cutoff of 520 eV to ensure a high precision in the calculations. It is known that DFT within the local-density approximation (LDA) or the generalized-gradient approximation (GGA) often yields incorrect results for systems with electrons with a small \( f \) orbital overlap and narrow \( f \) bands. The implementation of the DFT + \( U \) method has been found to improve the results in the study of cerium compounds.\(^{23}\) The exchange and correlation energies were described within the GGA in the PBEsol prescription.\(^{24}\) The GGA + \( U \) method was used to account for the strong correlation between the electrons in the Ce 4f shell on the basis of Dudarev’s method.\(^{25}\) In this method the on-site Coulomb interaction, \( U \) (Hubbard term), and the on-site exchange interaction \( J_H \) are treated together as \( U_{\text{eff}} = U - J_H \). For our GGA + \( U \) calculations we chose a value \( U = 6 \) eV and \( J_H = 1 \) eV for the Ce atom. These values were chosen by comparison with the electronic structure study of CeVO\(_4\) done by Da Silva et al.\(^{26}\) The Monkhorst–Pack scheme was employed for the Brillouin-zone (BZ) integrations\(^{27}\) with the grids \( 4 \times 4 \times 4, 4 \times 4 \times 2, \) and \( 4 \times 4 \times 3 \) for the zircon, scheelite, and monazite phases, respectively. In the relaxed-equilibrium configuration, the forces are less than 4 meV/\( \AA \) per atom in each of the Cartesian directions. Lattice-dynamics calculations of phonon modes were performed at the zone center (\( \Gamma \) point) of the BZ. The calculations provided information about the frequency, symmetry, and polarization vector of the vibrational modes in each structure. Highly converged results on forces are required for the calculation of a dynamical matrix of...
ZIRCON TO MONAZITE PHASE TRANSITION IN CeVO₄

IV. RESULTS

A. High-pressure XRD

At ambient conditions CeVO₄ crystallizes in the zircon phase (SG: I₄₁/amd, Z = 4). The zircon structure can be described by CeO₈ dodecahedrons with eight similar Ce-O distances and isolated VO₄ tetrahedrons (see Fig. 1). Figure 2 shows the selective XRD diffraction patterns of CeVO₄ at representative pressures. There were no noticeable changes in the diffraction pattern up to 4 GPa, and the diffraction peaks could be indexed to the zircon phase. At 5.5 GPa the appearance of many extra diffraction peaks was observed along with the weak remnant (112) diffraction peak of the zircon phase, as shown by the arrow in Fig. 2. These changes in the diffraction patterns are indicative of a structural phase transition in CeVO₄ at this pressure. The new diffraction peaks of CeVO₄ could be assigned to the monoclinic monazite phase (P2₁/n). On further increase of pressure the monazite phase was found to be stable up to 12 GPa, which is the highest pressure reached in our XRD measurements. On release of pressure the monazite phase was quenched, thus indicating the irreversible nature of the zircon-to-monazite phase transition. These results are in agreement with Raman measurements and calculations presented in the next sections.

The Rietveld refinement of all the background-corrected diffraction patterns was carried out using Powdercell software. The diffraction patterns up to 2$\theta$ = 18° were used to avoid any kind of gasket interference in the structural refinements. At ambient pressure the lattice parameters for zircon-structured CeVO₄ are refined as $a = 7.399$ Å and $c = 6.482$ Å, which are consistent with the Inorganic Crystal Structure Database (ICSD) card No. 66035. The lattice parameters and fractional coordinates of the zircon phase of CeVO₄ are given in Table I and are also in good agreement with those reported in previous HP and high-temperature XRD measurements by Range et al., a = 7.383 Å, c = 6.485 Å.

The pressure evolution of the lattice parameters and equation of state of CeVO₄ in the zircon and monazite phases is shown in Fig. 3. It can be seen that in the zircon phase the $a$ axis is more compressible than the $c$ axis, as is evident from the increase of the $c/a$ ratio from 0.878 at ambient pressure to 0.887 at 4 GPa. The linear compressibility of the $c$ axis ($K_c = 1.05 \times 10^{-3}$ GPa$^{-1}$) is smaller than that of the other two axes ($K_a = K_b = 3.48 \times 10^{-3}$ GPa$^{-1}$). These values are similar to those obtained in other zircon-type vanadates and related oxides. Due to deterioration of diffraction patterns in the monazite phase beyond 5.5 GPa, the value of $\beta$ angle refined at 5.5 GPa was kept constant for further refinements. A typical Rietveld refinement fit of diffraction data at 7.2 GPa is shown in Fig. 4, and the lattice parameters and fractional coordinates are presented in Table II. These parameters are in close agreement with lattice parameters reported in recent XRD measurements in monazite CePO₄. In the monazite phase we observed an irreversible nature of the zircon-to-monazite phase transition. The reason is that the monazite phase of CeVO₄ could be assigned to the monoclinic monazite structure of CePO₄ than that of CePO₄.

### Table I. Lattice parameters and fractional coordinates of CeVO₄

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*Intensity (arb. units)*

FIG. 2. Evolution of the XRD patterns of CeVO₄ as a function of pressure. Asterisks represent the diffraction peaks due to gasket. Arrow indicates the remnant (112) diffraction peak of the zircon phase.
is induced by pressure while that of CePO$_4$ occurs already at ambient pressure. Note that difference is found always when a HP monazite is compared with an ambient-pressure monazite. The zircon-to-monazite phase transition in CeVO$_4$ exhibits a volume collapse of 8.6% at 4 GPa which is quite large compared with those observed in orthophosphates. A fit of the volume vs. pressure data of the zircon phase to a second-order Birch–Murnaghan equation of state ($B'_0 = 4$) gives a bulk modulus of 118.9 GPa. This value is the smallest one found in orthovanadates, thus indicating that CeVO$_4$ is the most compressible orthovanadate to date. In the monazite phase, volume vs. pressure data fitted to a third-order Birch–Murnaghan equation of state give bulk moduli $B_0 = 142$ GPa and $B'_0 = 4.4$, which are relatively close to the bulk modulus of monazite-type CePO$_4$ ($B'_0 = 122$ GPa). During the fitting we excluded the pressure-volume data point collected at 12 GPa because it deviated from the systematic behavior of the rest of the data. A possible reason for this might be the assumption that the $\beta$ angle does not change under compression, which could lead to a unit-cell volume miscalculation.

The occurrence of the zircon-to-monazite transition instead of the zircon-to-scheelite transition is apparently in contradiction to the results reported by Range et al. These authors, who used a large-volume press, found that, upon compression at room temperature zircon-type CeVO$_4$ transforms to the scheelite phase. They observed the occurrence of the monazite phase only under the combined effect of pressure and

<table>
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<td>0.1268</td>
<td>0.2164</td>
<td>0.7108</td>
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</table>

TABLE II. Lattice parameters and fractional coordinates of CeVO$_4$ in the monazite phase at 5.5 GPa. SG $P2_1/n$, $Z = 4$, $a = 6.980$ Å, $b = 7.079$ Å, $c = 6.550$ Å, $\beta = 105.3^\circ$, and residuals $R_p = 32.46$, $R_{wp} = 37.99$. 

FIG. 3. Pressure dependence of the lattice parameters and volume. Filled circles (squares) correspond to the zircon (monazite) phase of CeVO$_4$. The solid lines in the lattice-parameter plots are linear fits of the data, and the solid lines in the volume data correspond to the third-order Birch–Murnaghan equation of state.

FIG. 4. Observed and calculated XRD diffraction patterns for the monazite ($P2_1/n$, $Z = 4$) phase of CeVO$_4$ at 7.3 GPa. Bars indicate the expected positions of diffraction peaks.
温度。为了证实这些结果，我们使用大型体积压机和布里奇曼 anvils 进行了类似实验。从不同压力下取样并进行 XRD 测量的结果如图 5 所示和表 III 中所示。我们的结果表明，锆石类型 CeVO₄ 在 4 GPa 的压力下转变为 scheelite 型，并在相同压力和接近 600 °C 的温度下转变为 monazite 型。这些结果确认了 Range 等人报道的结果。30 这两个实验的主要区别在于使用 DAC 和布里奇曼劵的压力介质。前者使用多轴应力，后者使用单轴应力。因此，我们的结果表明，锆石类型 CeVO₄ 在非水静压条件下转变为了 scheelite 型结构。高温度下，应力会变小，因此 monazite 型可以由 DAC 实验得到。值得注意的是，在布里奇曼劵实验中，monazite 型和 scheelite 型在不同压力下可以实现。表 IV 中列出了实验条件下 monazite 型和 scheelite 型的单胞参数和原子位置。为了便于比较，我们还给出了早期测量的单胞参数。30,33,34

### TABLE III. Results obtained from Bridgman-cell experiments.

<table>
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<th>Recovered sample phase</th>
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<td>Zircon</td>
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<td>4</td>
<td>Scheelite</td>
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<td>4</td>
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<td>Run 6</td>
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### B. Structural calculations

图 6(a)显示了三个不同结构的 CeVO₄ 总能量 (E) 随体积的变化。根据计算，ambient 压力条件下最稳定的相是锆石。计算得到的单胞参数、分数坐标和bulk模量列在表 V 中。这些值与实验值良好一致。monazite 型的 bulk modulus 稍有低估。特别是在低压锆石型中，计算得到的 B₀ 低 2%。thermodynamic 相变发生在两个结构的 Gibbs 自由能相等时。图 6(b)显示了 scheelite 和 monazite 型的 Gibbs 自由能随压力的变化。为了方便比较，我们还给出了早期测量的单胞参数和 scheelite 型的单胞参数。30,33,34

`FIG. 6. (Color online) (a) Variation of total energy, at T = 0 K, as a function of volume for zircon-, scheelite-, and monazite-type CeVO₄. Filled circles, squares, and triangles correspond to zircon, monazite, and scheelite phases, respectively. (b) Plot of the free energy, at T = 300 K, versus pressure for the scheelite and the monazite phases. The free energy of the zircon phase has been taken as a reference.`
TABLE IV. Lattice parameters of CeVO₄ in the scheelite phase and monazite phase obtained from Bridgman-cell compression with temperature variations. For comparison purpose lattice parameters reported by Range et al.⁴⁰ and Yoshimura and Sata⁴³ are also given.

<table>
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<tr>
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<td></td>
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<td></td>
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<td></td>
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<td>c = 11.848 Å</td>
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C. Raman scattering

1. Zircon-structured CeVO₄

At ambient conditions, CeVO₄ exists in the zircon structure (space group I₄₁/amd and point group D₄h) with two formula units per primitive cell. Group-theoretical analysis predicts 12 Raman-active modes 2A₁g + 4B₁g + B₂g + 5Eg. These modes can be further classified into internal (v₁-v₄) and external (translational T and rotational R) modes of VO₄ units as follows:

\[
\Gamma = A₁g(v₁, v₂) + B₁g(2T, v₃, v₄) + B₂g(v₃) + E₉(2T, R, v₃, v₄).
\]  (1)

Figure 7(a) shows the Raman spectra of CeVO₄ in the zircon phase at different pressures up to 4.5 GPa. Eight Raman modes have been observed at ambient condition out of 12 Raman peaks predicted for CeVO₄ in the zircon phase. The symmetry assignment for the Raman modes has been performed in accordance with our calculations and the comparison with previous results in other vanadates, and it is summarized in Table VI.

TABLE V. Calculated lattice parameters, bulk moduli, and fractional coordinates of CeVO₄ in the zircon phase at ambient conditions (SG I₄₁/amd, Z = 4, a = 7.423 Å, c = 6.461 Å, and the bulk modulus B₀ = 115.24 GPa, B′₀ = 4.83); in the monazite phase at 5.77 GPa (SG P₄₁/n, Z = 4, a = 6.869 Å, b = 7.119 Å, c = 6.56 Å, β = 104.88°, and the bulk moduli B₀ = 109.63 GPa, B′₀ = 3.24); and in the scheelite phase at ambient conditions. (SG I₄₁/a, Z = 4, a = 5.165 Å, and c = 11.795 Å, and the bulk moduli B₀ = 138.65 GPa, B′₀ = 3.84.)

<table>
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</table>

Table: Lattice parameters of CeVO₄ in the scheelite phase and monazite phase obtained from Bridgman-cell compression with temperature variations.
As can be seen from Fig. 7(a) and Table VI, the intense symmetric-stretching internal mode \( v_1(A_{1g}) \), observed at 864 cm\(^{-1} \) near ambient pressure exhibits the lowest frequency for this mode when compared with that of other rare-earth orthovanadates.\(^{38} \) This result suggests that CeVO\(_4\) exhibits the weakest intratetrahedral V-O bonds of all orthovanadates. The two asymmetric-stretching modes \( v_3(E_g) \) and \( v_3(B_{1g}) \) have been observed at 801 and 789 cm\(^{-1} \), respectively. Apart from these phonons of CeVO\(_4\), the four bending modes of the VO\(_4\) unit could be observed in the frequency range from 260 to 500 cm\(^{-1} \). However, we have observed only three bending modes \( [v_2(B_{2g}), v_2(A_{1g}), \text{and } v_4(B_{1g})] \), whose frequencies at ambient pressures are 262, 381, and 469 cm\(^{-1} \), respectively. The asymmetric-bending mode \( v_4(E_g) \) could not be detected. In most of the orthovanadates this mode remains undetectable.\(^{39–43} \) Similarly, out of the five external modes, two T(\( E_g \)) modes and one T(\( B_{1g} \)) mode have not been detected. These modes are absent probably due to their weak Raman-scattering cross sections.

Figure 7(b) shows the pressure dependence of Raman modes of CeVO\(_4\) in the zircon phase. The symmetry assignment for the Raman modes along with their experimental and calculated frequencies, pressure coefficients, and mode Grüneisen parameters (\( \gamma \)) are shown in Table VI. A very good agreement is found between experimental and theoretical results. The frequencies of almost all Raman-active modes of the zircon phase exhibit a positive pressure coefficient. The rotational mode has the highest Grüneisen parameter, being the mode most sensitive to changes of volume. In addition, the internal bending mode of \( v_2(B_{2g}) \) symmetry shows a negative pressure coefficient. A similar soft behavior was observed for the \( v_2(B_{2g}) \) mode in other orthovanadates, e.g., YVO\(_4\),\(^{39} \) YbVO\(_4\),\(^{41} \) LuVO\(_4\),\(^{42} \) ScVO\(_4\),\(^{40} \) and also in ScPO\(_4\).\(^{10} \) Our calculations also predict the softening of the T(\( E_g \)) mode with lowest frequency in CeVO\(_4\). This softening has been also observed in other orthovanadates and it could be a characteristic behavior of zircon-type compounds.\(^{39–42} \) It is important to note that the softening of both T(\( E_g \)) and \( v_2(B_{2g}) \) modes has been observed in compounds exhibiting the zircon-to-scheelite transition\(^{39–44} \) and also in those showing the zircon-to-monazite transition.\(^{7,10} \) Therefore, it indicates that the softening of both modes is a consequence of the instability of the zircon phase. We will discuss this issue in great detail in our discussion section.

As regards the values of the pressure coefficients of the Raman-active modes of the zircon-type orthovanadates, it is worth mentioning that the pressure coefficients of the internal stretching modes in CeVO\(_4\) are of the order of 4.9–5.5 cm\(^{-1} \)/GPa, which are in close comparison with those of other orthovanadates.\(^{39–44} \) Similarly, the pressure coefficients of the \( v_2(B_{2g}) \) bending mode are of the order of \(-1.2 \) as, it is among, those of other orthovanadates. Finally, it is interesting to note that the pressure coefficient of the rotational R(\( E_g \)) mode of CeVO\(_4\) has the smallest pressure coefficient of all known orthovanadates, thus indicating weak Ce–VO\(_4\) bonds compared with those of other orthovanadates.\(^{39–44} \)

FIG. 7. (a) Raman spectra of CeVO\(_4\) in the zircon phase between 0.5 and 4.5 GPa, (b) experimental pressure dependence of the Raman-mode frequencies in zircon-type CeVO\(_4\). The solid lines are the calculated modes. The dashed lines represent Raman modes not observed in the experiments.
TABLE VI. *Ab initio* calculated and experimental frequencies at ambient conditions (0.5 GPa), pressure coefficients, and mode Gr"uneisen parameters (γ) of the CeVO₄ in the zircon phase.

<table>
<thead>
<tr>
<th>Raman-mode Symmetry</th>
<th>$\omega_0^a$(cm⁻¹)</th>
<th>$d\omega$/dP$^a$ (cm⁻¹/GPa)</th>
<th>$\gamma^a$</th>
<th>$\omega_0^b$(cm⁻¹)</th>
<th>$d\omega$/dP$^b$ (cm⁻¹/GPa)</th>
<th>$\gamma^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(Eg)</td>
<td>110.5</td>
<td>−0.52</td>
<td>−0.63</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>T(B1g)</td>
<td>123.4</td>
<td>0.59</td>
<td>0.54</td>
<td>124.4</td>
<td>0.56</td>
<td>0.54</td>
</tr>
<tr>
<td>T(Eg)</td>
<td>153.0</td>
<td>0.66</td>
<td>0.57</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>R(Eg)</td>
<td>232.5</td>
<td>4.92</td>
<td>2.61</td>
<td>234.1</td>
<td>3.52</td>
<td>1.79</td>
</tr>
<tr>
<td>T(B1g)</td>
<td>236.7</td>
<td>2.92</td>
<td>1.58</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>$v_1$(B2g)</td>
<td>254.1</td>
<td>−1.18</td>
<td>−0.97</td>
<td>261.9</td>
<td>−1.25</td>
<td>−0.57</td>
</tr>
<tr>
<td>$v_3$(Eg)</td>
<td>354.6</td>
<td>0.42</td>
<td>0.20</td>
<td>381.1</td>
<td>0.12</td>
<td>0.04</td>
</tr>
<tr>
<td>$v_2$(A1g)</td>
<td>368.7</td>
<td>1.46</td>
<td>0.52</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>$v_4$(B1g)</td>
<td>451.4</td>
<td>2.27</td>
<td>0.65</td>
<td>468.9</td>
<td>2.26</td>
<td>0.57</td>
</tr>
<tr>
<td>$v_3$(B1g)</td>
<td>828.3</td>
<td>5.08</td>
<td>0.80</td>
<td>789.1</td>
<td>5.26</td>
<td>0.79</td>
</tr>
<tr>
<td>$v_1$(Eg)</td>
<td>828.7</td>
<td>5.41</td>
<td>0.85</td>
<td>801.3</td>
<td>4.95</td>
<td>0.73</td>
</tr>
<tr>
<td>$v_1$(A1g)</td>
<td>872.3</td>
<td>4.37</td>
<td>0.66</td>
<td>864.3</td>
<td>5.52</td>
<td>0.76</td>
</tr>
</tbody>
</table>

$^a$Theoretical calculations. $^b$Experimental data.

2. Monazite-structured CeVO₄

Raman-scattering measurements in CeVO₄ evidence that this compound undergoes a zircon-to-monazite phase transition above 5 GPa. Group-theoretical calculations for CeVO₄ in the monazite phase (SG: $P2_1/n$, point group $C_{2h}$) predict 36 vibrational Raman modes at the BZ center with the following symmetries: $\Gamma = 18A_g + 18 B_g$. These modes can be further classified into internal ($v_1$–$v_4$) and external (translational T and rotational R) modes of VO₄ units as follows:

$$\Gamma = A_g(6T, 3R, v_1, 2v_2, 3v_3, 3v_4) + B_g(6T, 3R, v_1, 2v_2, 3v_3, 3v_4)$$ (2)

Raman spectra of CeVO₄ in the monazite phase at selected pressures are shown in Fig. 8(a). At 5.3 GPa we have observed the appearance of several Raman bands, both in the range between 0 and 500 cm⁻¹ and between 700 and 1000 cm⁻¹, accompanied by the broadening of many Raman modes. These changes in the Raman spectra are indicative of a structural phase transition toward the lower-symmetry monoclinic monazite phase. This result is consistent with our XRD investigations and with previous results in orthophosphates. Out of 36 Raman-active modes in the monazite phase, we investigated and with previous results in orthophosphates. In general, the calculated Raman frequencies and their pressure coefficients are in good agreement with our experimental ones. The only mode whose assignment is doubtful is the soft mode observed at 89.6 cm⁻¹ at ambient pressure. This mode shows a frequency close to that of the calculated $A_g$ mode at 92.5 cm⁻¹ but its negative pressure coefficient is more similar to that of the calculated $B_g$ mode at 95.3 cm⁻¹.

Figure 8(b) shows the pressure dependence of the Raman-active modes of CeVO₄ in the monazite phase. All the experimental Raman-active modes show a positive pressure coefficient, except the two Raman modes at 89.6 and 140.4 cm⁻¹, which is in good agreement with our calculations that predict three soft modes. The pressure evolution observed for the Raman modes is similar to that reported for monazite CePO₄. Only the soft mode of $B_g$ symmetry calculated at 66.2 cm⁻¹ at ambient pressure was not measured. The softening of the same Raman modes was previously observed in TbVO₄. On release of pressure from 15.9 GPa to ambient pressure the monazite phase was recovered, thus showing the irreversible nature of the zircon-to-monazite phase transition in good agreement with our XRD results. It must be noted that a similar behavior was observed for TbPO₄.

3. Scheelite-structured CeVO₄

Group-theoretical calculations for CeVO₄ in the scheelite phase (SG: $I4_1/a$, point group $C_{4h}$) predict 13 vibrational Raman modes at the BZ center with the following symmetries: $\Gamma = 3A_g + 5B_g + 5E_g$. As already commented on, our theoretical calculations predict the possibility of the scheelite phase by comparing the experimental and calculated values of frequencies and pressure coefficients and is shown in Table VII together with the mode Gr"uneisen parameters (γ), calculated using the bulk modulus of the monazite phase, $B_0 = 131.5$ GPa, obtained from XRD measurements. The assignment of modes can be done broadly in two regions. The internal modes of the vibration of VO₄ tetrahedra cover the frequency range of 290–950 cm⁻¹, while the external modes of VO₄ unit span the frequency range of 50–270 cm⁻¹. This assignment is consistent in comparison with orthophosphates. In general, the calculated Raman frequencies and their pressure coefficients are in good agreement with our experimental ones. The only mode whose assignment is doubtful is the soft mode observed at 89.6 cm⁻¹ at ambient pressure. This mode shows a frequency close to that of the calculated $A_g$ mode at 92.5 cm⁻¹ but its negative pressure coefficient is more similar to that of the calculated $B_g$ mode at 95.3 cm⁻¹.
ZIRCON TO MONAZITE PHASE TRANSITION IN CeVO$_4$

Raman shift (cm$^{-1}$)

5.3 GPa
13.5 GPa
12.2 GPa
9.3 GPa
7.3 GPa
5.3 GPa

Pressure (GPa)

0 2 4 6 8 10 12 14 16 18

Raman frequency (cm$^{-1}$)

0 100 200 300 400 500 600 700 800 900 1000

FIG. 8. (a) Raman spectra of the monazite phase of CeVO$_4$ at pressures between 5.3 and 15.9 GPa. (b) Experimental pressure dependence of the Raman-mode frequencies in monazite phase CeVO$_4$. Filled and empty squares correspond to Raman modes in monazite CeVO$_4$ on upstroke and downstroke, respectively. The solid lines are the calculated modes. The dashed lines represent Raman modes not observed in the experiments.

V. DISCUSSION

Zircon-structured orthovanadates under hydrostatic compression were observed to undergo the zircon-to-scheelite and then the scheelite-to-fergusonite phase transitions. In all cases, the scheelite phase was found to be quenchable on release of pressure. The zircon-to-scheelite phase transition is a rather sluggish first-order and reconstructive transition in nature while the scheelite-to-fergusonite transition is a ferroelastic second-order and displacive transition. In our case, the zircon-to-scheelite transition involves a volume collapse of 11%, which is consistent with the first-order character of the transformation. On the other hand, the zircon-to-monazite phase transition is a rather sudden transition with a volume collapse of 8%, with an increase of the Ce$^{3+}$ coordination and without the coexistence of phases over a wide pressure range (typical of the zircon-to-scheelite transition). All these facts indicate the first-order and reconstructive nature of this phase transition. The structural relationships between monazite and zircon were elucidated by Ni et al. These relationships can be used to understand the reconstructive nature of the zircon-to-monazite phase transition with the help of Fig. 1. In monazite, CeO$_9$ polyhedra share edges and corners with an isolated VO$_4$ tetrahedra, whereas in Zircon it is CeO$_8$ dodecahedra that share edges and corners. The edger sharing VO$_4$ and CeO$_8$ polyhedral chains along the [001] direction of the zircon structure appears to be like polyhedral chains in monazite, although the chains are twisted to accommodate the ninth atom. However, due to the extra ninth oxygen atom, the packing efficiency in the monazite phase is better compared with that of the zircon phase. This result supports the observed higher bulk modulus value for monazite CeVO$_4$. This new atomic arrangement in the monazite phase can be realized by considering a slight shift of the [001] planes and a rotation of VO$_4$ polyhedra in the $a$-$b$ plane. The fact that this transition (as well as the zircon-to-scheelite transition) is not reversible is a notable aspect. We think that a large kinetic barrier is the cause of nonreversibility, which is consistent with the reconstructive mechanism of this transition and its first-order character. Another important issue to remark is that the presence of AO$_9$ polyhedra (a cationic pentagonal interpenetrating tetrahedral polyhedral) allows monazite to accommodate chemically
diverse cations. The irregular coordination around the A cation does not place severe symmetry, size, or charge constraints and allows large domains of chemical composition. Therefore, we predict that, in addition to CeVO₄, other zircon-structured vanadates with large A cations could also take the monazite structure under pressure, becoming isostructural to LaCrO₄.

An important issue related to the fact that under compression the zircon structure becomes mechanically unstable is the softening of external translational T(E₂g) and internal ν₂(B₂g) bending modes. In zircon-structured compounds, the softening of the T(E₂g) mode is related to a softening of the C₆₆ elastic constant. This fact is caused by monoclinic distortions in the a-c or b-c planes. Similarly, the softening of the ν₂(B₂g) mode is related to a softening of the C₆₆ elastic constant, which is caused by orthorhombic distortions in the basal plane. Low-temperature studies of zircon-structured DyVO₄, DyAsO₄, and TbVO₄ indicate a similar phonon softening which can be attributed to the distortion of the zircon structure along the [110] or [100] direction. By analogy, the pressure-induced contraction would lead to similar distortions in the zircon structure, making this structure unstable.

To contribute to the systematic understanding of structural properties of zircon-type oxides, here we will make the attempt to understand the factors which govern the phase stability at ambient pressure and the sequence of pressure-induced structural phase transitions in orthovanadates and orthophosphates. As commented on earlier, the phase stability of zircon-type orthovanadates and orthophosphates and their phase transitions seem to greatly depend on the ionic radii. This is consistent with the recent updated version of Bastide's diagram for ABX₄ compounds, elaborated on and discussed by Errandonea and Manjón. In Bastides diagram, the phase stability and phase transitions of ABO₄ orthovanadates and orthophosphates can be understood by considering the role

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**TABLE VII.** Theoretical and experimental frequencies, pressure coefficients, and mode Grüneisen parameters of monazite CeVO₄.

<table>
<thead>
<tr>
<th>Raman-mode Symmetry</th>
<th>ωₐ (cm⁻¹)</th>
<th>dω/dP (cm⁻¹/GPa)</th>
<th>γa</th>
<th>ωb (cm⁻¹)</th>
<th>dω/dP (cm⁻¹/GPa)</th>
<th>γb</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₈</td>
<td>66.2</td>
<td>−0.58</td>
<td>−1.11</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>A₅</td>
<td>73.5</td>
<td>0.51</td>
<td>0.82</td>
<td>72.1</td>
<td>0.35</td>
<td>0.69</td>
</tr>
<tr>
<td>A₃</td>
<td>92.5</td>
<td>0.27</td>
<td>0.35</td>
<td>89.6</td>
<td>−0.31</td>
<td>−0.49</td>
</tr>
<tr>
<td>B₈</td>
<td>95.3</td>
<td>−1.20</td>
<td>−1.61</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>A₅</td>
<td>107.3</td>
<td>0.01</td>
<td>0.01</td>
<td>104.2</td>
<td>0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>B₈</td>
<td>121.6</td>
<td>1.35</td>
<td>1.30</td>
<td>126.3</td>
<td>0.55</td>
<td>0.62</td>
</tr>
<tr>
<td>B₈</td>
<td>126.4</td>
<td>1.28</td>
<td>1.18</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
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<td>−0.30</td>
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<td>140.4</td>
<td>−0.69</td>
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<tr>
<td>A₅</td>
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<td>1.67</td>
<td>1.32</td>
<td>146.5</td>
<td>1.26</td>
<td>1.22</td>
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<td>1.69</td>
<td>161.8</td>
<td>0.95</td>
<td>0.83</td>
</tr>
<tr>
<td>A₃</td>
<td>160.7</td>
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<td>1.68</td>
<td>−</td>
<td>−</td>
<td>−</td>
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<tr>
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<td>193.4</td>
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<td>−</td>
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<td>A₅</td>
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<td>243.8</td>
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</tr>
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<td>1.12</td>
</tr>
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<td>771.2</td>
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<td>0.53</td>
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<td>0.31</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

*Theoretical calculations.

*Experimental data.*
played by cationic radii, $r_A$ and $r_B$, with respect to anion radius, $r_O$. In this diagram, those compounds which have $r_A/r_O$ and $r_B/r_O$ cation-to-anion ratios well inside the stability region of the zircon structure are observed to undergo the zircon-to-scheelite phase transition and follow the traditional north-east (NE) rule in Bastide's diagram. Such is the case of many zircon-structured orthovanadates, like YVO$_4$, YbVO$_4$, LuVO$_4$, and also in ScPO$_4$. On the other hand, those compounds whose $r_A/r_O$ and $r_B/r_O$ cation-to-anion ratios fall near the border of the stability region of the zircon and monazite structures could crystallize in both phases, like CeVO$_4$, TbPO$_4$, and YPO$_4$. In this case, the compounds crystallizing in the zircon phase, like CeVO$_4$, are prone to undergo the zircon-to-monazite phase transition. A few orthophosphates, like YbPO$_4$ and LuP$_2$O$_7$, are exceptions to this rule and deserve further investigation. Finally, the last case would correspond to compounds whose $r_A/r_O$ and $r_B/r_O$ cation-to-anion ratios fall well inside the stability region of the monazite phase. This is the case for most orthophosphates, which already crystallize in the monazite phase. To conclude we would like to add that the crystal chemistry arguments here used to discuss the structural behavior of phosphates and vanadates has been recently satisfactorily use to describe arsenates and chromates.

Finally, we would like to comment on additional consequences of the observed pressure-driven structural changes. CeVO$_4$ is a large-bandgap material with a bandgap energy of 3.1–4.2 eV. It is usually assumed that the electronic structure near the Fermi level is dominated by V 3d and O 2p states. However, recently a bandgap of 1.8 eV was measured and attributed to the presence of localized 4f levels of Ce between the valence and conduction bands. Clearly there is a contradiction between both pictures of the electronic band structure which could be solved by HP optical-absorption studies like those already preformed in PbWO$_4$. It is known that pressure affects differently localized and delocalized electronic states. In particular, if 4f states are present near the Fermi level, we expect $E_g$ to be considerable reduced by pressure within the stability range of the zircon structure. In addition, both the zircon-to-scheelite and zircon-to-monazite transitions will probably cause a large collapse of the bandgap as a consequence of the atomic rearrangement after the phase transitions. Finally, another issue interesting to explore in the future are the effects caused by HP electron delocalization of lanthanides, which, among other things, should modify the magnetic properties of compounds like CeVO$_4$.

VI. CONCLUSION

XRD, Raman-scattering, and theoretical studies of CeVO$_4$ up to 16 GPa suggests that the low-pressure zircon phase undergoes an irreversible zircon-to-monazite phase transition at 5.3 GPa. XRD and Raman signals weaken considerably beyond 12 and 16 GPa, respectively, evading any further measurements. The symmetries of the Raman modes in the zircon and monazite phases of CeVO$_4$ have been assigned in accordance with our lattice-dynamics calculations. In general, good agreement is found for the zircon-to-monazite phase transition by our experimental and theoretical data. Our calculations predict the monazite-to-scheelite phase transition, which could not be detected experimentally under hydrostatic conditions. However, the scheelite structure is observed upon compression under nonhydrostatic conditions. The softening of external translational T(E$_g$) and internal v$_2$(B$_2g$) bending modes can be attributed to distortion in the zircon structure along the [110] or [100] direction associated with the phase transition. We have also discussed the dependence of the phase stability of the zircon phase and its pressure-induced phase transitions either to the scheelite or monazite phases in orthovanadates and orthophosphates on their $r_A/r_O$ and $r_B/r_O$ cation-to-anion ratios. Finally, the effects of nonhydrostaticity in the structural sequence are discussed. We found that different compression methods induced a transition to different structures.

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*Corresponding author.
