High-Pressure Phase Transition of Micro- and Nanoscale HoVO₄ and High-Pressure Phase Diagram of REVO₄ with RE Ionic Radius

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ABSTRACT: In situ Raman spectra of HoVO₄ micro- and nanocrystals were obtained at high pressures up to 25.4 and 18.0 GPa at room temperature, respectively. The appearance of new peaks in the Raman spectra and the discontinuities of the Raman-mode shift provided powerful evidence for an irreversible zircon-to-scheelite structure transformation for HoVO₄ microcrystals at 7.2 GPa and for HoVO₄ nanocrystals at 8.7 GPa. The lattice contraction caused by the size effect was thought to be responsible for the different phase-transition pressures. Also, the higher stability of HoVO₄ nanocrystals compared with the microcrystals was also confirmed using the Raman frequencies and pressure coefficients. The results of the phase transition of HoVO₄ were compared with previously reported rare-earth orthovanadates, and the phase diagram of REVO₄ with RE ionic radius at different pressures was presented.

INTRODUCTION

Rare-earth vanadates (REVO₄) have numerous applications such as catalysts, phosphors, polarizers, and laser materials because of their excellent electric, optical, and magnetic properties. Recently, synthesis and characterization of REVO₄ nanomaterials have been of considerable interest because of their novel size-dependent properties. At the same time, high-pressure research on nanomaterials has attracted much attention for the appearance of many novel high-pressure behaviors in the nanomaterials. The size effect in high-pressure research has attracted great interest considering that the grain size at the nanoscale level can distinctly influence the material properties under high pressure. Therefore, high-pressure study of the size-dependent structural stability of REVO₄ is also considered important. Among all of the rare-earth vanadates, only LaVO₄ nanocrystals were studied under high pressure in previous reports. Unfortunately, the high-pressure research of bulk LaVO₄ has not been conducted. It means that there is not even one rare-earth vanadate where high-pressure experiment was conducted for nanomaterials and bulk materials under the same conditions.

HoVO₄, as a typical rare-earth vanadate, has some excellent properties compared with other REVO₄ materials, such as the best catalytic performance for the oxidative dehydrogenation of ethane. Although a number of studies about REVO₄ under high pressure have been reported, there are a few reports on the high-pressure study of HoVO₄, specifically size-dependent HoVO₄. High-pressure XRD experiments on HoVO₄ were conducted by Garg et al. at pressures up to 28 GPa, and the zircon–scheelite transition phase-transition pressure was found to be located at 4.5 and 8.2 GPa under nonhydrostatic and quasi-hydrostatic conditions, respectively. In their experiments, Ar and a methanol–ethanol (4:1) mixture were used as pressure-transmitting medium (PTM) to obtain quasi-hydrostatic and nonhydrostatic pressures, respectively. The high-pressure Raman spectra of bulk HoVO₄ were studied by Chen et al., and a zircon–scheelite transition at 9.3 GPa was observed, although their experiment was conducted without any PTM. However, they did not conduct the size-dependent high-pressure research on HoVO₄.

Most REVO₄ crystals exist in the zircon-type structure (space group I₄₁/amd) under ambient conditions and undergo a phase transition to the scheelite-type structure (space group I₄₁/a) under compression. However, there are also a few REVO₄ compounds, like CeVO₄, that undergo a direct zircon-to-monazite phase transition under high pressures. Therefore, to better understand the size-dependent structural stability of REVO₄ and also the high-pressure properties of HoVO₄, the present work aims at the in situ Raman spectroscopy study of HoVO₄ micro- and nanocrystals under high pressures at room temperature. The irreversible phase transition is found for HoVO₄ crystals under high pressures. On the basis of this, we further explore the common rule for phase transformation of all rare-earth vanadates.

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RESULTS AND DISCUSSION

Structure of HoVO₄. The XRD diffraction patterns of the synthesized HoVO₄ micro- and nanocrystals are shown in Figure 1. All of these diffraction peaks of the micro- and nanocrystals agree with the JCPDS card 15-0764; the result indicates that pure zircon-type micro- and nanocrystalline HoVO₄ structures were obtained. Compared with the microcrystal data, the diffraction peaks of nanocrystals were apparently broadened because of the finite size of the crystallites, which is known as Debye–Scherrer broadening. The XRD patterns of these two samples were well refined by Rietveld analysis as the red lines in Figure 1 show. The well-fitted XRD patterns demonstrated that the prepared HoVO₄ crystallizes in a triclinic structure with the space group $I\overline{4}1/m$ without impurity. Crystal unit-cell parameters were calculated by the Rietveld method using the MAUD software.

The unit-cell parameters of the microcrystals ($a = 7.110$ Å, $b = 7.110$ Å, and $c = 6.281$ Å) and nanocrystals ($a = 7.110$ Å, $b = 7.110$ Å, and $c = 6.264$ Å) in this work are very similar with the bulk HoVO₄ data ($a = 7.121$ Å, $b = 7.121$ Å, and $c = 6.293$ Å) obtained from references. The refined crystallographic data clearly indicate a reduction in the lattice parameters with a decreased crystal size, especially in the direction of the crystallographic axis $c$. For nanocrystals, there exists an extra pressure caused by the surface tension at the crystallite surface. For a sphere-shaped particle with a radius of $r$, the pressure intensity distribution on the particle is linearly associated with $1/r$ and is indirectly proportional to the surface-to-volume ratio. Considering this, the extra pressure caused by the surface tension exerted on a smaller grain is apparently higher than that of the pressure exerted on a larger one. Therefore, a distinct lattice contraction occurs when the crystallite size decrease from microscale to nanoscale. Figure 2a,b shows the SEM image of the HoVO₄ microcrystals and the TEM image of the HoVO₄ nanocrystals, respectively. The microcrystals have a length of $\sim 1$ μm and a width of $\sim 300$ nm, and the nanocrystals have a diameter of $\sim 20$ nm.

Raman Modes of HoVO₄ under Ambient Conditions. Under ambient conditions, HoVO₄ crystallizes in the zircon-type structure just like many other REVO₄ materials. Group theoretical calculations predicted that there are 12 first-order Raman modes in the Brillouin zone center with symmetries: 20

$$\Gamma = 2A_4 + 4B_5 + B_2 + 5E_1$$  \hspace{1cm} (1)

The Raman spectra of micro- and nanocrystalline HoVO₄ in the zircon-type phase under ambient conditions were collected and displayed at the bottom of Figures 3 and 4, respectively. In our experiment, only 8 of 12 Raman active modes are clearly discernible under ambient conditions, which agree well with the previous report. 20 Among them, the Raman modes located in the range of 260–900 cm$^{-1}$ are internal modes ($\nu_1$ to $\nu_4$) attributed to the antisymmetric stretching vibrations of the V–O bond within the VO₄ tetrahedra, and the modes located in the range of 100–260 cm$^{-1}$ are external modes ($T$ and $R$). The Raman active modes of HoVO₄ microcrystals and nanocrystals

Figure 1. XRD patterns of the prepared micro- and nanocrystalline HoVO₄.

Figure 2. (a) SEM image of microcrystalline HoVO₄ and (b) TEM image of nanocrystalline HoVO₄.

Figure 3. Raman spectra of microcrystalline HoVO₄ under high pressure. Asterisks (*) represent the Raman modes of silicon oil as the pressure-transmitting medium.

Figure 4. Raman spectra of nanocrystalline HoVO₄ under high pressure. Asterisks (*) represent the Raman modes of silicon oil as the pressure-transmitting medium.

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under ambient conditions with the corresponding mode assignments from ref 20 are listed in Table 1. The corresponding data of single crystals are also shown in Table 1 for comparison. It can be clearly seen that almost all Raman frequencies of nanocrystals HoVO₄ are a little bit higher than those of the microcrystals. This can be understood by considering the influence of crystalline grain size on the force constants of the nearest-neighbor bonds.24,25 When the grain size of HoVO₄ decreased to the nanometer scale, the interatomic distances decreased. As a consequence, the Raman modes shift toward a higher frequency.

**Pressure Effects on Microcrystalline HoVO₄** Figure 3 shows the Raman spectra of microcrystalline HoVO₄ under high pressure up to 25.4 GPa at room temperature. Below 7.2 GPa, all Raman peaks can be identified with the HoVO₄ zircon-type structure except the signals of silicon oil, and the pressure coefficient of each Raman mode calculated by using a linear fit is listed in Table 1. No significant change in the Raman pattern occurred during this compression process, but most Raman peaks shifted toward higher frequencies with increased pressure, except the internal $\nu_2(B_{1g})$ mode at 261 cm⁻¹ and the external $T(E_g)$ mode at 156 cm⁻¹. The softening of these two modes, which was caused by orthorhombic distortions in the basal plane and monoclinic distortions in the $a$-$c$ or $b$-$c$ planes, respectively,24,25 was also observed in many other REVO₄ materials under high pressure.22,28,29,30 It should be noted that they are not classical soft modes, of which the frequency usually approaches zero accompanied by some specific kind of phase transition. The results obtained from $TmPO₄$, which also has a zircon-type structure, indicated that the classical soft mode can be assigned to the R(B₁₉g) mode. Further, the lattice-dynamics calculations showed that this silent mode is caused by the rotation of the rigid PO₄ tetrahedra.27

When the pressure was increased to 7.2 GPa, some remarkable changes occurred in the Raman pattern. Several new peaks appeared at frequencies of 142, 190, and 372 cm⁻¹, which can be assigned to the $T(B_{1g})$, $T(E_g)$, and $\nu_2(B_{1g})$ modes of a scheelite-type structure, respectively. The intensity of these new Raman peaks increased gradually with increasing pressure, whereas the characteristic peaks of the zircon-type HoVO₄ became more and more indistinct. These variations shown on the Raman pattern of HoVO₄ microcrystals confirmed a pressure-induced structure transformation from zircon-type to scheelite-type, which was similar to the phenomenon observed in YVO₄.28 ScVO₄,28 GdVO₄,29 and LuVO₄.30 In the unit cell of the scheelrite structure of HoVO₄, including four formula units, the V atoms occupy S₄ sites of the VO₄ group. Under the C₄h point group corresponding to Γ, the factor group analysis predicts that there are 13 zone-center Raman active modes:31,32

$$\Gamma = \nu_1(A_g) + \nu_2(A_g) + \nu_3(B_{2g}) + \nu_3(E_g) + \nu_4(B_{1g}) + \nu_4(E_g) + R(A_g) + R(E_g) + 2T(B_{2g}) + 2T(E_g)$$

(2)

In this work, we displayed only six modes considering that the remaining Raman modes are too weak to distinguish because of the broadening and degeneracy of Raman peaks under high pressure. The pressure dependences of the Raman frequencies of HoVO₄ microcrystals are plotted and linear-fitted in Figure 5. Also, the discontinuities of the Raman frequencies with increased pressure can be easily distinguished at 7.2 GPa, which means that a pressure-induced structure transformation starts at this pressure. The Raman frequencies and their pressure coefficients calculated by using linear fit are listed in Table 2.

After releasing the pressure under ambient conditions, the Raman spectra collected after decompression cannot be assigned to zircon-type. However, they cannot be assigned to the scheelrite phase as well. Considering this, we believe that a third polymorph or a mixture of phases is obtained after

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**Table 1. Raman Frequencies, Mode Assignments, and the Pressure Derivatives of Zircon-Type Micro- and Nanocrystalline HoVO₄**

| mode type | microcrystal | nanocrystal | single crystals |
|-----------|--------------|-------------|----------------|
|           | $\omega_0$ (cm⁻¹) | $d\omega_0/dP$ (cm⁻¹/GPa) | $\omega_0$ (cm⁻¹) | $d\omega_0/dP$ (cm⁻¹/GPa) | $\omega_0$ (cm⁻¹) |
| $T(B_{1g})$ | 119 | 0.9 | 120 | 1.1 | 119 |
| $T(E_g)$ | 156 | −1.2 | 158 | −0.1 | 156 |
| $\nu_2(B_{1g})$ | 261 | −1.2 | 263 | −0.7 | 261 |
| $\nu_2(A_{1g})$ | 383 | 1.9 | 385 | 2.0 | 380 |
| $\nu_2(B_{1g})$ | 488 | 2.7 | 489 | 2.8 | 487 |
| $\nu_1(B_{1g})$ | 816 | 5.5 | 817 | 5.7 | 816 |
| $\nu_1(B_{1g})$ | 833 | 5.3 | 836 | 5.5 | 834 |
| $\nu_1(A_{1g})$ | 891 | 5.7 | 893 | 5.9 | 891 |

$T = \text{external translation and } \nu = \text{internal}.$

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**Table 2. Raman Frequencies, Mode Assignments, and the Pressure Derivatives of Scheelite-Type Micro- and Nanocrystalline HoVO₄**

| mode type | microcrystal | nanocrystal |
|-----------|--------------|-------------|
|           | $\omega_0$ (cm⁻¹) | $d\omega_0/dP$ (cm⁻¹/GPa) | $\omega_0$ (cm⁻¹) | $d\omega_0/dP$ (cm⁻¹/GPa) |
| $T(B_{1g})$ | 142 | 0 | 145 | −0.2 |
| $T(E_g)$ | 190 | 1.6 | 203 | 0.2 |
| $R(A_{1g})$ | 253 | 1.1 | 257 | 0.4 |
| $\nu_2(B_{1g})$ | 372 | 3.0 | 379 | 2.4 |
| $\nu_1(B_{1g})$ | 394 | 1.4 | 401 | 0.1 |
| $\nu_1(A_{1g})$ | 856 | 3.5 | 866 | 2.4 |

$T = \text{external translation, } R = \text{external rotation, and } \nu = \text{internal}.$
decompression. This behavior has also been found in ScVO₄ and GdVO₄.³³,³⁴ Thus, it can be concluded that at room temperature, HoVO₄ microcrystals undergo an irreversible zircon-to-scheelite structure transformation at a pressure of 7.2 GPa. After decompression, a third polymorph or a mixture of phases is obtained.

**Pressure Effects on Nanocrystalline HoVO₄.** Figure 4 shows the in situ Raman spectra of HoVO₄ nanocrystals with increasing pressure at room temperature. The Raman shifts for the peaks of nanocrystalline HoVO₄ under pressure are similar to those of microcrystalline HoVO₄. All peaks can be identified as zircon-type structures below 8.7 GPa. Also, the pressure coefficients of the zircon-type Raman modes were calculated by linear fits, which are shown and presented in Figure 6 and Table 1. At 8.7 GPa, two new broad and weak peaks were observed at 145 and 379 cm⁻¹, which can be assigned to the T(Bg) and ν₂(Bg) modes of scheelite-type structure, respectively. Another new Raman peak at 202 cm⁻¹ that can be assigned to the T(Eg) mode of scheelite-type appeared when the pressure was increased to 11.7 GPa. The intensity of these new Raman peaks all became stronger gradually with increasing pressure, whereas the zircon-type Raman peaks lose their intensity slowly and became indistinct and broad. The discontinuities of Raman frequencies with increasing pressure indicated a clearly pressure-induced structure transformation at 8.7 GPa. The Raman frequencies with their mode assignments and pressure coefficients of scheelite-type HoVO₄ are listed in Table 2.

When the pressure was released under ambient conditions, the Raman frequencies were consistent with those of the scheelite-structure HoVO₄, which emerged under high pressure. Thus, the structure transformation of HoVO₄ nanocrystals is also irreversible. In conclusion, HoVO₄ nanocrystals undergo an irreversible zircon-to-scheelite structure transformation at a pressure of 8.7 GPa at normal temperature, which is similar to the pressure-induced structure transformation observed in HoVO₄ nanocrystals. A third polymorph or a mixture of phases is obtained after decompression.

**Size-Dependent Phase-Transition Pressures of HoVO₄.** After studying the high-pressure properties of the micro- and nanocrystalline HoVO₄, we compared our results with the previous experiments conducted on bulk HoVO₄. In the experiment conducted by Garg et al., the irreversible zircon–scheelite transition was found at 4.5 and 8.2 GPa under nonhydrostatic and quasi-hydrostatic conditions, respectively.¹⁴ The phase-transition pressure of microcrystalline and nanocrystalline HoVO₄ obtained in this work is 7.2 and 8.7 GPa, respectively, which is closer to the results obtained under the quasi-hydrostatic conditions. It should be pointed out that the difference in crystal size, measurement methods (XRD or Raman), and pressure-transmission medium can all influence the final phase-transition pressure. Considering this, the difference in the phase-transition medium can be understood. Chen et al. conducted Raman measurements on bulk HoVO₄ and found that the zircon–scheelite transition occurred at 9.3 GPa.³⁵ Their results are not far from the phase-transition pressure obtained in this work. However, they did not use any PTM in their experiments. In that case, the phase-transition pressure should be treated with caution.

According to the results of the above experiments, it is clear that HoVO₄ nanocrystals possess a higher phase-transition pressure compared to microcrystalline and bulk materials. The phase-transition pressures for various REVO₄ materials as a function of RE cation ionic radius (r(RE)) are listed in Table 3. The pressure dependences of the Raman frequencies of HoVO₄ nanocrystals are plotted in Figure 6. The discontinuities of Raman frequencies with increasing pressure indicated a clearly pressure-induced structure transformation at 8.7 GPa. The Raman frequencies with their mode assignments and pressure coefficients of scheelite-type HoVO₄ are listed in Table 2.

**Table 1.** At 8.7 GPa, two new broad and weak peaks were observed at 145 and 379 cm⁻¹, which can be assigned to the T(Bg) and ν₂(Bg) modes of scheelite-type structure, respectively. Another new Raman peak at 202 cm⁻¹ that can be assigned to the T(Eg) mode of scheelite-type appeared when the pressure was increased to 11.7 GPa. The intensity of these new Raman peaks all became stronger gradually with increasing pressure, whereas the zircon-type Raman peaks lose their intensity slowly and became indistinct and broad. The pressure coefficients of the zircon-type Raman modes were calculated by linear fits, which are shown and presented in Figure 6 and Table 1.

**Table 3.** Phase-Transition Direction and Pressure for Various REVO₄ Materials as a Function of RE Cation Ionic Radius (r(RE))

| element | ionic radius (Å) | nanocrystal phase-transition pressure (GPa) | microcrystal/bulk phase-transition pressure (GPa) | transition direction |
|---------|-----------------|------------------------------------------|-----------------------------------------------|---------------------|
| La      | 1.03            | 5.9⁴³                                    | 5.9⁴³                                         | zircon to monazite  |
| Ce      | 1.02            | 5.6⁴⁴                                    | 5.6⁴⁴                                         | zircon to monazite  |
| Pr      | 0.99            | 6.0⁴⁵                                    | 6.0⁴⁵                                         | zircon to monazite  |
| Nd      | 0.98            | 6.0⁴⁵/6.5⁵⁵                              | 6.0⁴⁵/6.5⁵⁵                                   | zircon to monazite  |
| Pm      | 0.97            | 6.5⁴⁵                                    | 6.5⁴⁵                                         | zircon to scheelite |
| Sm      | 0.96            | 6.5⁴⁵                                    | 6.5⁴⁵                                         | zircon to scheelite |
| Eu      | 0.95            | 6.8⁴⁵/7.8⁵⁸                              | 6.8⁴⁵/7.8⁵⁸                                   | zircon to scheelite |
| Gd      | 0.94            | 7.4⁴⁹                                    | 7.4⁴⁹                                         | zircon to scheelite |
| Tb      | 0.92            | 6.4⁴⁵/6.7⁵⁰                              | 6.4⁴⁵/6.7⁵⁰                                   | zircon to scheelite |
| Dy      | 0.91            | 6.5⁴⁵/8.0⁵²                              | 6.5⁴⁵/8.0⁵²                                   | zircon to scheelite |
| Ho      | 0.90            | 8.7 [this work]                          | 8.7 [this work]                               | zircon to scheelite |
| Y       | 0.90            | 8.5⁴⁵/7.5⁵⁰                              | 8.5⁴⁵/7.5⁵⁰                                   | zircon to scheelite |
| Er      | 0.89            | 8.0⁴³                                    | 8.0⁴³                                         | zircon to scheelite |
| Tm      | 0.88            | 7.3⁴⁶                                    | 7.3⁴⁶                                         | zircon to scheelite |
| Yb      | 0.87            | 8.0⁴⁰                                    | 8.0⁴⁰                                         | zircon to scheelite |
| Lu      | 0.86            | 8.2⁴⁵/8.7⁴⁸                              | 8.2⁴⁵/8.7⁴⁸                                   | zircon to scheelite |
| Sc      | 0.75            | 8.2⁴⁵/8.7⁴⁸                              | 8.2⁴⁵/8.7⁴⁸                                   | zircon to scheelite |
pressure compared with the microcrystals. To understand this, it is worth noting that Table 1 indicates that not only almost all of the Raman frequencies but also all of the pressure coefficients of nanocrystals are higher than those of the microcrystals. It is safe to say that the strength of most bonds of HoVO$_4$ is increased when the crystalline grain size is decreased from the micrometer to nanometer scale. Generally, when the particle size decreased, the size-induced radial pressure leads to the decrease in lattice constant.\textsuperscript{36} Apparently, HoVO$_4$ crystals comply with this rule. This has been confirmed from the higher Raman frequencies of nanocrystals, as compared with the HoVO$_4$ microcrystals described above. Thus, the structural stability is increased, resulting in a higher phase-transition pressure.

RE Ionic Radius-Dependent Phase Transition of REVO$_4$.

It is known that many REVO$_4$ undergo a phase transition from zircon-type to scheelite-type under low GPa such as HoVO$_4$, GaVO$_4$, and so on, while a few of them transform into monazite-type such as LaVO$_4$ and CeVO$_4$. To explore the influence factor behind this phenomenon, we summarized the phase-transition direction and pressures of different REVO$_4$ materials with their RE ionic radius as shown in Table 3. Considering that the properties of microcrystals are very close to those of bulk materials, we listed them in one row in Table 3. We noted that when the RE ionic radius is below 0.97 Å, the corresponding REVO$_4$ would likely undergo a phase transition from zircon-type to scheelite-type; otherwise, it will transform into monazite-type. This is an interesting conclusion, which has not been straightforwardly proposed in previous reports as far as we know. Furthermore, phase-transition pressures of all these REVO$_4$ materials as a function of RE ionic radius are shown in Figure 7. It is clear that the lower the RE ionic radius is, the higher the phase transition pressure. Whether it was a phase transition into scheelite or monazite, both apply to this conclusion. The relationship between phase-transition pressure and RE ionic radius can be described approximately by this formula:

$$P_T = 9.41 - 0.01 \exp(5.81R)$$ \hspace{1cm} (3)

Combined with this fit result, we can draw the phase diagram of REVO$_4$ at different pressures and with different RE ionic radii as seen in Figure 7. The zircon phase is more stable in REVO$_4$ with a small RE ionic radius. When the pressure is below the line of eq 3, REVO$_4$ tends to exist in zircon-type. After increasing the pressure, REVO$_4$ would transform into scheelite-type if it has a small RE ionic radius and, otherwise, to monazite-type. The boundary is located at 0.97 ± 0.01 Å. According to eq 3, TmVO$_4$ is predicted to undergo zircon-to-scheelite phase transitions at about 7.8 GPa. Previously, our prediction for the phase transition of ErVO$_4$ has been proved by a very recent work published by Javier et al.\textsuperscript{37} The phase-transition pressure of PmVO$_4$ are predicted to be around 6.5 GPa, whereas the transition direction is not sure because it is just located at the critical point of scheelite and monazite phase.

### CONCLUSIONS

The high-pressure Raman spectra of micro- and nanocrystalline HoVO$_4$ were obtained at room temperature. The appearance of new peaks in the Raman spectra and the discontinuities of the Raman-mode shift provided powerful evidence for an irreversible zircon-to-scheelite structure transformation for HoVO$_4$ microcrystals at 7.2 GPa and for HoVO$_4$ nanocrystals at 8.7 GPa, which indicates that the phase-transition pressure of HoVO$_4$ increases with the reducing particle size. The higher stability of nanocrystals of HoVO$_4$ was confirmed by the higher Raman frequencies and pressure coefficients compared with the nanocrystals. Combined with the high-pressure study on EuVO$_4$, we infer that the phase-transition pressure of other REVO$_4$ micro- and nanocrystals should also comply with this rule. Additionally, we summarized previous work on high-pressure study on REVO$_4$ and obtained a high-pressure phase diagram of REVO$_4$ with RE ionic radius. According to this phase diagram, the high-pressure properties of ErVO$_4$, TmVO$_4$, and PmVO$_4$ were predicted. Among which, the predictions for ErVO$_4$ are in excellent agreement with the recently published work on high-pressure XRD experiments.

### EXPERIMENTAL SECTION

The micro- and nanocrystalline HoVO$_4$ materials were prepared by a hydrothermal method based on the previous literature.\textsuperscript{38,39} For example, in the synthesis procedure of nanocrystalline HoVO$_4$, first, 0.28 mmol of Ho$_2$O$_3$ was dissolved in 10.0 mL of 1 mol/L HNO$_3$. Ho(NO$_3$)$_3$ crystals were produced after the excess HNO$_3$ was removed. Then, 30 mL water was added to dissolve the Ho(NO$_3$)$_3$ crystals. Afterward, a homogeneous Na$_3$VO$_4$ aqueous solution produced by mixing 0.28 mmol of V$_2$O$_5$ powders with dilute NaOH solution was dropwise added into the Ho(NO$_3$)$_3$ solution. After quickly stirring for 10 min, the homogeneous mixture was poured into a 50 mL Teflon-lined autoclave. Then, the autoclave was sealed up and treated at 200 °C for 24 h. Afterward, the precipitates were collected after centrifugation at 3500 rpm for 15 min and washed with ethanol and deionized water. Finally, the product was obtained.

The crystal structures of the samples were identified by X-ray diffraction apparatus (TTRAX3) with Cu K$_\alpha$ radiation ($\lambda = 1.542$ Å). The grain size of the samples was surveyed using a scanning electron microscope (JSM-6700F) and transmission electron microscope (JEOL-2010). A diamond anvil cell (DAC) with a stainless steel gasket was used to generate high pressure. A circular hole with a diameter of 160 μm was drilled into the gasket center by a spark driller, which was used to place the sample. The pressure was determined by the widely adopted ruby fluorescence method.\textsuperscript{40} To avoid uneven pressure within the sample, silicon oil was used as the pressure-
transmitting medium. It should be stated that silicon oil is known not to be quasi-hydrostatic beyond 10 GPa. Klotz et al. indicated that pressure differences increase with pressures up to 6 GPa. However, this pressure difference was smaller than 0.4 GPa when the pressure was below 12 GPa. The traditional pressure-transmitting media, a methanol–ethanol mixture and a methanol–ethanol–water mixture, will lead to changes of the Raman modes of HoVO₄. The silicon oil has no influence on the Raman signal of the samples, so it was employed as the pressure-transmitting medium. In situ Raman signals were collected by a confocal microscope Raman spectrometer system (Horiba Jobin Yvon LabRAM HR), which is equipped with a multichannel air-cooled CCD detector and a stigmatic spectrometer, excited by a 514.5 nm Ar⁺ laser with an incident power of 5.4 mW, and all Raman spectra were collected in the reflection geometry at normal temperature. The resolution of the applied Raman system is 2 cm⁻¹.

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**Notes**

The authors declare no competing financial interest.

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