Optical properties and structural phase transitions of W-doped VO$_2$(R) under pressure

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We investigated the optical properties and structural phase transitions of W-doped VO$_2$(R) nanoparticles under pressure based on in situ synchrotron X-ray diffraction (XRD) and infrared (IR) spectroscopy. The structural transition sequence follows VO$_2$(R)→VO$_2$(CaCl$_2$-type)→VO$_2$(Mx) and VO$_2$(Mx)→VO$_2$(Mx') within metallic phases, in compression and decompression processes, respectively, demonstrating that the structural transition can be decoupled from the metal-insulator transition (MIT). VO$_2$(R) and VO$_2$(CaCl$_2$-type) exhibit expected behavior of increased metallicty under pressure; surprisingly, VO$_2$(Mx) shows gradually decreased metallicty with increasing pressure and VO$_2$(Mx') is still metallic under ambient conditions. We find that the reduced metallicty of VO$_2$(Mx) is attributed to W-doping induced local structure distortion in the high-pressure region, while the metallic properties of VO$_2$(Mx') are associated with the enhancement of electron concentration due to the presence of W donors, which shifted the Fermi level toward the conduction band. The present results demonstrate that the structural transition is not the key factor in driving the metal-insulator transition, and provide an effective method for inducing MIT in VO$_2$(Mx').

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a corundum structure into a monoclinic phase, the corundum-
to-monoclinic transformation occurs between two metallic
phases under pressure, demonstrating that the structural
transition can be decoupled from the MIT. These results
suggest the possibility of decoupling MIT from structural
transition in metallic VO$_2$(R) phase under pressure, however, no
efforts have been performed on the electrical study on the
metallic VO$_2$(R) under pressure.

As is known, the R-to-M1 transition temperature ($T_c$) can
be reduced by doping with transition metal, such as W$^{6+}$, Mo$^{6+}$,
and Nb$^{5+}$. Among these, the most exciting prospective way
would be the W-doping, which enabling precise and wide range
control of $T_c$, with a nearly linear reduction rate of 18.4–26 °C/
atom$^{-1}$, providing experimental base for high pressure
research on VO$_2$(R). Infrared spectroscopy, as a powerful tool to
probe the dynamics of charge carriers, has been widely used in
the high-pressure study on strong correlated materials. In this
study, we present the measurements of infrared properties
and structure phase transitions of W$^{6+}$VO$_2$(R) to 63.9 GPa. We found a pressure induced rutile–orthorhombic–
monoclinic transitions in three metallic phases, and obtained
a metallic W–VO$_2$(MX) (W–VO$_2$(MX')) at ambient conditions.

**Experimental**

**Synthesis**

W–VO$_2$(R) nanoparticles were synthesized through hydro-
thermal reaction combined with subsequent calcinations. In
a typical procedure, 0.2275 g V$_2$O$_5$, 0.3938 g oxalic acid and
0.0824 g Na$_2$WO$_4$·2H$_2$O were added to 100 ml deionized water,
and followed by vigorous stirring until a pale-yellow solution
was formed. The solution was transferred into a Teflon-lined
autoclave with the filling ratio of 0.6, and held at 190 °C for
24 h. The precipitate was collected by centrifugal separation,
was washed with deionized water and alcohol and dried in vacuum
freezing dryer. The resulted powers were calcined at 600 °C for
3 h in argon atmosphere.

**Characterization**

Samples were characterized using transmission electron
microscopy (TEM) (200 KV, HITACHI, H-81001V), and high-
resolution transmission electron microscopy (HRTEM) (JEOL
JEM-3010). High-pressure XRD and IR experiments were carried
out by using diamond anvil cells (DACs). The T301 stainless-
steel gaskets were preindented to 40–50 μm and drilled with
a center hole of ~100 μm as sample chamber. High-pressure
XRD use a 4:1 methanol–ethanol mixture as pressure-
transmitting medium. High-pressure IR measurements were
carried out using pure sample. The ruby fluorescence technique
was used to calibrate pressures for all experiments. The *in situ*
high pressure synchrotron XRD measurements were performed
at the BL15U beamline of Shanghai Synchrotron Radiation
Facility (SSRF) ($\lambda = 0.6199$ Å). The high-pressure IR spectra
were collected through a Bruker Vertex 80V FTIR spectrometer and
a microscope/a Hyperion 2000 IR microscope equipped with
a liquid nitrogen cooled MCT detector.

The optical reflectivity of sample–diamond interface $R_{sd(\omega)}$
was obtained by the following equation:

$$ R_{sd(\omega)} = \frac{I_{sd(\omega)}}{I_{d(\omega)}} \frac{I_{d(\omega)}}{I_{0(\omega)}} \quad (1) $$

where $I_{sd(\omega)}$ and $I_{d(\omega)}$ are the intensities reflected from
the sample–diamond interface and the air–diamond interface at
each pressure, respectively. $I_{e(\omega)}$ and $I_{d(\omega)}$ are the intensities
reflected from empty cell and air–gold foil interface, respectively.

**Results**

**Pressure-dependent IR spectra**

The characterizations for the structure and morphology of
synthesized W-doped samples are shown in Fig. S1† all the
diffraction peaks can be indexed to VO$_2$(R), indicating that the
W-doped samples are pure VO$_2$(R) nanoparticles with average
diameter of 100–200 nm. To investigate the electronic changes
for W–VO$_2$(R) nanoparticles under pressure, we performed high
pressure mid-IR reflectivity $R_{sd(\omega)}$ spectra measurements
(shown in Fig. 1). The data between 1700 cm$^{-1}$ and 2700 cm$^{-1}$
were cut out from $R_{sd(\omega)}$ spectra due to the absorption of dia-
mond. At ~1.9 GPa, $R_{sd(\omega)}$ is slightly lower than expected for
sample–air interface due to the larger refractive index value in
diamond. With increasing pressure, $R_{sd(\omega)}$ gradually

![Fig. 1 IR reflectivity spectra of W–VO$_2$ nanoparticles upon compression in the pressure region of (a) 1.9–30.2 GPa and (b) 30.2–68.2 GPa, (c) pressure-reflectivity diagram of three different wave numbers (3300, 3500 and 3000 cm$^{-1}$) upon compression. IR reflectivity spectra of W–VO$_2$ nanoparticles upon decompression in the pressure region of (d) 68.2–35.7 GPa and (e) 32.1–11 GPa, (f) pressure-reflectivity diagram for three different wave numbers (3300, 3500 and 3000 cm$^{-1}$) upon decompression.](image-url)
increases up to 12.8 GPa, and then shows almost no change in the 12.8–30.2 GPa range. Surprisingly, $R_{sd}(\omega)$ starts to decrease above 30.2 GPa, and then decrease more subtle when the pressure is beyond 53.6 GPa. This unexpected behavior above 30.2 GPa has not been observed in VO$_2$ system before. According to early study, the reflectivity in terms of dielectric constant ($\sqrt{\varepsilon(\omega)}$) at normal incidence is given by$^{45}$

$$R(\omega) = \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \quad (2)$$

The $\sqrt{\varepsilon(\omega)}$ has the following form

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\omega_p} + \sum_{i=1}^{n} \frac{s_i}{\omega^2 - \omega_i^2 - i\Gamma_i\omega} \quad (3)$$

where $\varepsilon_{\infty}$ represents a contribution to the real part of $\varepsilon(\omega)$ from high-frequency electronic transitions, $\frac{\omega_p^2}{\omega^2 + i\omega\omega_p}$ represents the contribution to $\varepsilon(\omega)$ from free-electron, $\omega_p$ and $\omega_c$ are the carrier density parameter and collision frequency, respectively. The last term is the sum over Lorenz, classical oscillators that contribute to the nonconstant part of $\varepsilon(\omega)$. In low-frequency, the reflectivity of the R phase is characterized by a continues rise due to the free-electronic contribution.$^{46,47}$ The higher reflectivity in low-frequency region, indicates higher carrier density in measured samples. Therefore, the pressure dependence of the IR reflectivity at low frequencies gives the electronic evolution under pressure, qualitatively. As shown in Fig. 1c, the reflectivity at low frequencies increases gradually owing to a larger bandwidth up to 12.8 GPa, but show a noticeable change in slope at about 12.8 GPa, which could be related to the structural phase transition of VO$_2$(R)-to-VO$_2$(CaCl$_2$-type) observed in early XRD study on pure VO$_2$(R).$^{39}$ When pressure is above 30.2 GPa, the reflectivity starts to decrease, but then decreases more sluggish with further compressing above 53.6 GPa, suggesting the metallicity decreases in W–VO$_2$ under higher pressure. These results show pressure makes our sample more metallic only up to 30.2 GPa. According to early study, the IR spectroscopy decisively depends on the configuration of atoms,$^{48}$ therefore, the unexpected decrease of IR reflectivity should be mainly related to the accompanying change in crystal structure under pressure.

Upon decompression, $R_{sd}(\omega)$ exhibits subtle change up to 17.4 GPa (Fig. 1d and e). With further decompressing, $R_{sd}(\omega)$ starts to decrease significantly. When the applied pressure decreased to 1.1 GPa, the reflectivity is clearly lower than that of initial W–VO$_2$(R) phase (Fig. 1a and e). Similar behaviors are observed in the pressure-reflectivity diagram for wave numbers at 1300, 3500 and 3000 cm$^{-1}$. These results suggest that the metallicity is independent with pressure above 17.4 GPa, but decreases with pressure upon further decompressing.

For clarifying that whether W–VO$_2$ nanoparticles in different pressure regions are metallic or not, we carried out high pressure transmittance spectra measurements on both W–VO$_2$ and pure VO$_2$ (shown in Fig. 2). The data between 1700 cm$^{-1}$ and 2700 cm$^{-1}$ were cut out from $R_{sd}(\omega)$ spectra due to the absorption of diamond. Compared with the transmittance spectra of the insulating VO$_2$(M1) and the quenched VO$_2$(Mx) in pure VO$_2$ (inset of Fig. 2), which present maxima in IR transmittance at around 1000 cm$^{-1}$, there is no transmitted light in the whole spectrum in W–VO$_2$ under various pressures. These results clearly identify that W–VO$_2$ is metallic in whole pressure region.

Pressure-dependent XRD patterns

To have a better understanding of the changes in the metallicity of W–VO$_2$(R) under pressure, we carried out high pressure XRD measurements in characterizing the crystal structural transition up to 63.9 GPa (shown in Fig. 3). In the low pressure range (0–13.5 GPa), all diffraction peaks shift toward smaller $d$-spacings.

**Fig. 2** IR transmittance spectra of W–VO$_2$ nanoparticles at selected pressures. Inset: IR transmittance spectrum of insulating M1 and Mx phases in pure VO$_2$.

**Fig. 3** XRD patterns of W–VO$_2$(R) nanoparticles at various pressures, (a) collected upon compression, (b) collected upon decompression. Diffraction peaks marked *”, #” and “*” originate from VO$_2$(CaCl$_2$-type), VO$_2$(Mx) and Fe, respectively. The lines at the bottom of (a) correspond to the diffraction peaks of VO$_2$(R) taken from PDF no. 79-1655.
due to lattice compression, without modifications of the overall diffraction pattern. Above 13.5 GPa, some diffraction peaks start to broaden or split (denoted by stars), indicating a structural transition from R into an orthorhombic CaCl₂-type phase, which is consistent with previous study on pure VO₂(R). With further increasing pressure above 31.3 GPa, several new peaks (marked with “*”) appear, suggesting the occurrence of the structural transition from CaCl₂-type phase into a new high-pressure phase. At 63.9 GPa, the CaCl₂-type phase completely transforms into the new high-pressure phase. The structure of the high-pressure phase is still unclear. The diffraction pattern of the high-pressure phase is clearly different from that of X phase in bulk VO₂, but similar to that of the Mx phase in VO₂ nanoparticles (Fig. 4a). Therefore, a monoclinic unit cell with space group P2₁/c was used to fit the measured XRD pattern at 63.9 GPa. As shown in Fig. 4b, the fitting gives relatively satisfying results, with $R_{wp} = 0.48\%$, $R_p = 0.36\%$. The lattice parameters are listed in Table 1. Note that the onset and pressures of the structural transition from the CaCl₂-type to the high-pressure Mx phase agree well with the pressures of the slope change in IR reflectivity (Fig. 1c). This indicates the electric change of W-VO₂ depends on its structural transition behaviors under high pressure.

Upon decompression, a new peak appears at ~3.09 Å when the pressure decreases to ~44.0 GPa, indicating a structural transition from VO₂(Mx) phase into a new structure (shown in Fig. 3b). With further decreasing pressure, all the diffraction peaks of VO₂(Mx) phase gradually weaken and finally disappear at ~21.7 GPa, showing that all the VO₂(Mx) samples transform into the new phase. We note that this structural transition process is rather sluggish, with the two phases coexist spanning over 20 GPa, demonstrating that this structural transformation is kinetically hindered. The XRD pattern of the released sample is similar to that of Mx' phase in pure VO₂ nanoparticles (shown in Fig. 4c), therefore, a monoclinic structure with the same space group P2₁/c were used to refine it. The results of Rietveld refinements are shown in Fig. 4d, with $R_{wp} = 0.50\%$, $R_p = 0.35\%$, and the obtained cell parameters are listed in Table 1. Both of the cell parameters and cell volume $V$ are close to those of pure counterparts, suggesting that W-doping induces only subtle modifications in crystal structure of the released sample. It is interesting that the quenched W-VO₂ samples are metallic at ambient conditions. Thus, these results demonstrate the W-doping induced MIT in VO₂(Mx) without structural phase transition. The structural phase transitions of rutile–orthorhombic and monoclinic–monoclinic in metallic phases in compressing and decompressing processes, respectively, and the doping-induced MIT in VO₂(Mx) indicate that the structural transition can be decoupled from MIT.

### Discussion

The pressure dependence of reflectivity in the R phase (Fig. 1c) indicates that pressure makes the R phase more metallic. Within the 0–13.5 GPa range, the isotropic compression in the R phase resulted in a continuous decrease in cell volume (Fig. 3). So the W-VO₂(R) follows the expected behavior of increased metallicity due to larger bandwidth. In the pressure range of 12.8–30.2 GPa, the reflectivity is high and show subtle changes within the crystal structure of the CaCl₂-type phase, indicating that CaCl₂-type phase show better metallicity than the R phase. It is worth noting that the metallicity gradually decreases with further compressing above 30.2 GPa, accompanied with a structural transformation from the CaCl₂-type phase into the high-pressure Mx phase, indicates that the high-pressure Mx phase in W-VO₂ nanoparticles is less metallic. As the W–Mx phase has the same crystal structure with pure the Mx phase, we made a comparison on the metallicity of these samples (shown in Fig. 5). The reflectivity of the W–Mx is much lower than that of the pure Mx, suggesting that the W-doping makes Mx phase less metallic. Although the W–Mx and pure Mx phases show similar XRD patterns, we note that the diffraction peaks in the W–Mx phase is broader and weaker than that of the pure Mx phase (Fig. 4a), moreover, the lattice parameter $c$ and the cell volume $V$ of the W–Mx phase are larger than that of pure Mx phase (Table 1). These results suggest that W-doping induced disorder of local structure was probably formed in W-Mx. According to previous study, the W-doping induced disorder in VO₂(R) results in an obvious increase in resistivity. So the poor

### Table 1 Parameters for Mx and Mx’ phases in W doped and pure VO₂ nanoparticles

<table>
<thead>
<tr>
<th>Phase</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-Mx</td>
<td>4.434</td>
<td>4.741</td>
<td>4.918</td>
<td>102.645</td>
<td>This study</td>
</tr>
<tr>
<td>Mx</td>
<td>4.468</td>
<td>4.693</td>
<td>4.744</td>
<td>98.699</td>
<td>Ref. 32</td>
</tr>
<tr>
<td>W-Mx’</td>
<td>4.681</td>
<td>5.324</td>
<td>6.336</td>
<td>154.792</td>
<td>This study</td>
</tr>
<tr>
<td>Mx’</td>
<td>4.631</td>
<td>5.308</td>
<td>6.394</td>
<td>151.820</td>
<td>Ref. 32</td>
</tr>
</tbody>
</table>

Fig. 4 The XRD patterns of (a) W–VO₂(Mx) nanoparticles, VO₂(Mx) nanoparticles and bulk VO₂(X), (c) W–VO₂(Mx’) and VO₂(Mx’) nanoparticles. Refinement results of (b) W–VO₂(Mx) nanoparticles at 63.9 GPa, (d) W–VO₂(Mx) nanoparticles at ambient pressure.
metallicity in the W-Mx phase is likely related to W-doping induced disorder of local structure.

Upon decompression, the structural transition from the W-Mx to W-Mx' phase starts from ~44 GPa and completed at about 21.7 GPa, whereas the metallicity is independent of applied pressure above 17.4 GPa, suggests that the metallicity of these two phases are stable in the high pressure region. When released to ambient pressure, the W-Mx' phase shows remarkable decreased metallicity but is still metallic, in contrast to the insulator Mx' phase in pure VO₂ nanoparticles (shown in the inset of Fig. 2). These results indicate that W-doping induced MIT occurs in the Mx' phase. Compared with the W-doping induced MIT in M1 phase, which accompanied with a structural transformation from the M1 to R phase, the MIT in the Mx' phase occurs without structural transition. Previous studies have indicated that the presence of W donors enhance the electron concentration in VO₂, which could shift the Fermi level toward conduction band and resulting in the MIT. These results not only pave an effective method for modifying electronic properties of VO₂ new structure, but also provide further insight into the MIT of VO₂.

Conclusion

We have investigated the structural phase transitions and optical properties on W-doped VO₂(R) nanoparticles under pressure. Compared with the temperature-dependent study on VO₂, where rutile–monoclinic structural transition always coincides with MIT, the structural transitions of rutile–orthorhombic–monoclinic occur within metallic phases under pressure. Moreover, we find a W-doping induced MIT in VO₂(Mx') without structural transitions. We suggest that the decreased metallicity in Mx phase under pressure can be attributed to the W-doping induced local structure distortion, and the MIT of Mx' phase may results from the enhancement of electron concentration due to the presence of W donors, which shifted the Fermi level toward the conduction band. Present results demonstrate that structural transition is not the key factor in driving metal-insulator transition, and paves an effective method for modifying electronic properties of VO₂ new structure.

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References
