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Pressure-induced phase transitions and insulator-metal transitions in VO_2 nanoparticles

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ABSTRACT

We present pressure-induced phase transitions and metallization in VO_2 nanoparticles characterized by synchrotron x-ray diffraction, Raman spectroscopy, and infrared reflectivity measurements. The *M1-M1′-Mx* phase transitions were found in VO_2 nanoparticles upon compression. The results of IR reflectivity shown that pressure-induced metallization occurs in the *M1′* phase with increasing pressure and the sample becomes fully metallic at the transition of *M1′ to Mx*. The metallic *Mx* phase transforms to metastable mixed phases displaying insulating properties upon decompression. We attribute the pressure-induced metallization of the *M1′* phase to the strong electron correlations, while the metal-insulator transition (MIT) from the *Mx* to the mixed phases is found to be associated with the structural phase transitions. Both the electron-correlation-driven Mott transition and the structure-driven MIT can be achieved in VO_2 by applying pressure. Compared with bulk samples, the VO_2 nanoparticles exhibit larger bulk moduli and increased transition pressure due to their nanosize effects. High pressure provides an effective method to study the MIT in strongly correlated materials and paves the way for modifying electronic properties of VO_2.

1. Introduction

As a typical strongly correlated electron material, VO_2 has attracted considerable attention because of its reversible metal-insulator transition (MIT) at a moderate temperature of ~340 K, which is accompanied by a phase transition from a metallic rutile (*R*) phase at high temperatures to an insulating monoclinic (*M1*) phase at low temperatures [1–4]. Across the transition, VO_2 exhibits an abrupt change in electrical, magnetic and optical properties, making VO_2 an important material for smart optical, electrical and thermal switches [1–6]. Therefore, the underlying physics of the MIT is essential for various applications, which has been widely studied [1–10]. Various mechanisms, such as Mott transition [11–13], Peierls transition [14,15], and combinations of these two [16,17] have been proposed for explaining the temperature-induced MIT in VO_2. The exact nature of the underlying physics remains an active subject of debate, largely because of difficulties in decoupling the structural transition and electron correlation. Recently, high pressure was introduced to study VO_2 as an effective means, providing a way to correlate crystal structure with electronic properties and/or to decouple the electronic and structural phase transitions [6,18–23]. Some previous studies have shown that both structural phase transitions and the MIT can be achieved by pressure [18–22]. Pressure-induced metallization (PIM), different from the *M1-R* phase transition driven by temperature, was found in monoclinic VO_2 above 10 GPa [18]. High pressure x-ray diffraction (XRD) studies have shown that the metallic phase is isostructural with the starting *M1* phase [21]. These results do not support the Peierls distortion and emphasize the role of electron-electron correlation in the MIT. In addition, photo-induced metallization was observed in monoclinic VO_2 without changes in the lattice symmetry under high pressure, indicating that the MIT is driven by the strong electron correlations [6]. More recently, the phase transition from a monoclinic to another monoclinic structure in VO_2 at ~10 GPa was explained by a semiconductor-to-semiconductor transition using high pressure *in situ* resistivity measurements [22,23]. Bai et al. [22] also pointed out that the high

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pressure monoclinic (*M1′*) phase is not metallic, and found a new high pressure metallic *X* phase above 34.3 GPa. They suggested that the structural transition dominates the pressure-induced insulator-to-metal transition in VO_2. Thus, contradictory conclusions regarding the mechanism of the MIT remain, in particular it is not clear whether structural phase transition or strong electron correlations play the dominant role in the MIT.

It is well known that domain structures greatly influence the properties of some strongly correlated materials [24,25]. In some previous studies of VO_2, it was considered an obstacle for clearly understanding the microscopic mechanism of the MIT [26–29]. In contrast to the bulk materials, the sizes of nanomaterials can be smaller than the characteristic domain size, such that nanomaterials can be utilized as a model system for exploring fundamental properties of VO_2 without influence from domain structures [24,27,28]. In addition, nanosized materials show various excellent properties and unique behaviors [25,30–32]. Therefore, several efforts have been made to study the MIT in VO_2 nanomaterials [24–29,33–36]. For instance, the relationship between the structural domain formation and the MIT in VO_2 nanobeams was investigated by Raman spectroscopy; a monoclinic and correlated metal phase was observed preceding the appearance of the rutile metallic phase [27]. VO_2 in ordered arrays exhibited size-dependent multipole optical resonance and transition temperatures, indicating the MIT temperature and the width of the hysteresis loop decreases with increasing particle size [34]. Surface stress mediated the Mott MIT in single-crystal VO_2 nanowires, for which the Mott insulating (*M2*) phase is critical in controlling the spatial extent and distribution of the insulating monoclinic and metallic rutile phases as well as the electrical characteristics of the transition [35]. However, the pressure effects on phase transition and the MIT in VO_2 nanomaterials are still poorly understood.

In this paper, we have studied pressure-induced phase transitions and insulator-metal transitions in VO_2 nanoparticles by synchrotron XRD, Raman spectroscopy, and infrared (IR) reflectivity spectra. *M1-M1′-Mx* phase transitions were observed upon compression, and the *Mx* phase transforms into mixed phases upon decompression.

2. Experimental

VO_2 nanoparticles with irregular morphology were synthesized through hydrothermal reaction combined with subsequent calcinations as described in a previous report [37]. The minimum dimension of the irregular nanoparticles is in the range of 100–200 nm. High pressure powder XRD experiments were performed at 16-IDB beamline of the High Pressure Collaborative Access Team (HPCAT) facility, at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), and BL15U beamline of Shanghai Synchrotron Radiation Facility (SSRF). High pressure experiments were carried out in a diamond-anvil cell (DAC) with 300 μm diameter culets and rhenium as gasket material. Neon was used as pressure transmitting medium. Pressure was determined by the frequency shift of the ruby R1 fluorescence line and equation of state (EOS) of Au. The incident wavelength of the monochromatic beam was 0.4066 Å. Raman measurements were carried out using a Renishaw spectrometer with Ar^+ excitation laser (wavelength of 514.5 nm). The recovered sample from high pressure was characterized again by XRD after approximately one week. Le Bail whole-profile fits of the XRD patterns were performed using the GSAS software package [38].

The IR reflectivity spectra were collected by a Bruker Vertex 80v FTIR spectrometer and a microscope equipped with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. The VO_2 slabs were obtained by pressing the VO_2 nanoparticles between the diamond anvils. The sample slabs were placed on top of a pre-indented KBr pellet in the sample chamber. KBr and ruby were used as pressure-transmitting medium and pressure gauge, respectively. The reflectivity of sample-diamond interface (R(ω)) was calculated by the following equation:

$$R(\omega) = \frac{I_R^S(\omega)}{I_R^{Air}(\omega)} \cdot \frac{I_R^{D\prime}(\omega)}{I_R^D(\omega)}$$

where $I_R^S(\omega)$ is the intensity reflected by the sample-diamond interface at each pressure, and $I_R^D(\omega)$ is the intensity reflected by the external face of the diamond anvil at each working pressure. $I_R^{Air}(\omega)$ and $I_R^{D\prime}(\omega)$ are the intensity reflected by air-diamond interface and by the external face of the diamond anvil, respectively.

3. Results and discussion

Fig. 1 shows the evolution of XRD patterns of VO_2 nanoparticles with increasing pressure. All the observed diffraction peaks can be indexed with the *M1* monoclinic structure below 14.9 GPa. All the diffraction peaks of the *M1* phase shifted to higher angles with increasing pressure, consistent with decreasing volume of the unit cells. Above this pressure, some diffraction peaks start to broaden or split as denoted by stars, indicating an isostructural phase transition from *M1* to *M1′* occurring above 15 GPa. The *M1′* phase is a distorted *M1* structure with the same space group ($P2_1/c$), which is consistent with the previous studies [21,22]. However, the phase transition pressure of the nanoparticle sample is higher than those (12–13 GPa) of the corresponding bulk samples [21,22]. Likely, nanosize contributed to the enhanced transition pressure because of the increased surface energy as observed in most nanomaterials [34–36]. With further increasing pressure, several new peaks appear at 32.2 GPa as marked with hash signs, which indicate a new

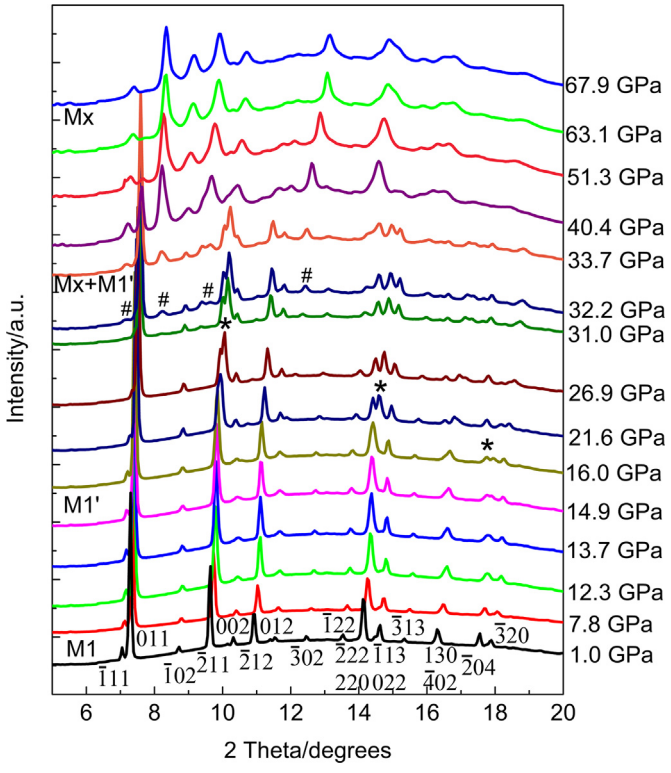

Fig. 1. High pressure XRD patterns of VO_2 nanoparticles. Stars and hash signs indicate typical diffraction peaks from the *M1′* and *Mx* phases, respectively.