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RAPID COMMUNICATION

Neutron powder diffraction and high-pressure synchrotron x-ray diffraction study of tantalum nitrides*

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Tantalum nitride (TaN) compact with a Vickers hardness of 26 GPa is prepared by a high-pressure and high-temperature (HPHT) method. The crystal structure and atom occupations of WC-type TaN have been investigated by neutron powder diffraction, and the compressibility of WC-type TaN has been investigated by using *in-situ* high-pressure synchrotron x-ray diffraction. The third-order Birch–Murnaghan equation of state fitted to the x-ray diffraction pressure–volume (P–V) sets of data, collected up to 41 GPa, yields ambient pressure isothermal bulk moduli of $B_0 = 369(2)$ GPa with pressure derivatives of $B_0' = 4$ for the WC-type TaN. The bulk modulus of WC-type TaN is not in good agreement with the previous result ($B_0 = 351$ GPa), which is close to the recent theoretical calculation result ($B_0 = 378$ GPa). An analysis of the experiment results shows that crystal structure of WC-type TaN can be viewed as alternate stacking of Ta and N layers along the c direction, and the covalent Ta–N bonds between Ta and N layers along the c axis in the crystal structure play an important role in the incompressibility and hardness of WC-type TaN.

Keywords: neutron powder diffraction, synchrotron x-ray diffraction, TaN, high pressure

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1. Introduction

Tantalum nitrides are attractive materials for making wear-resistant coatings and as diffusion barriers for copper in semiconductor devices.[1,2] Their outstanding heat resistance, chemical stability, and hardness also make them potentially useful as industrial materials.[3–5] In particular, tantalum mononitride (TaN), at least has three structures, an ambient CoSn-type (P-62m) phase,[6] a high-pressure WC-type phase (space group P-6m2),[7,8] and a high-pressure NaCl-type phase (space group Fm-3m).[9,10] When starting from CoSn-type TaN, Boiko and Popova reported that the WC-type TaN could be obtained at the pressure (3 GPa–10 GPa) and the temperature (673 K–2073 K), and the NaCl-type TaN could be obtained at above 2073 K in the same pressure conditions,[11] which were also consistent with experiment results by Brauer *et al*.[12] Sequentially, a density functional theory (DFT) calculation predicted that the WC-type TaN should be a potential hard alloy as hard as WC with the hardness up to 37.1 GPa.[13] A recent theoretical work indicated that the bulk modulus of the WC-type TaN could be up to 378 GPa.[14] However, a recent experimental study on this material showed that the Vickers hardness of the obtained WC-type TaN bulk only reached 11 GPa with $B_0 = 351(1)$ GPa.[15] Whether or not the WC-type TaN is a potential hard material as hard as WC ($H_v > 20$ GPa) is not known. In addition, TaN is an interstitial compound with variable amounts of nitrogen atoms. It is the high valence electron density and covalent bond that enhance the hardness of Ta significantly, because the hardness of pure Ta is only 0.9 GPa.[16] Previous theoretical works predicted that the powerful covalent bonding between the Ta atom and its neighboring N atoms may play an important role in strengthening the crystal structure to increase the hardness of the compound,[13] and Ta atoms would contribute high valence electron density to enhance incompressibility of WC-type TaN.[17–19] However, there is still no experimental investigation on the origin of the incompressibility of WC-type TaN as far as we are aware and no evidence indicates that it is a hard material. It stimulates us to further explore crystal structure and compressibility of WC-type TaN under high pressure.

Neutron powder diffraction is a unique and powerful probe for precisely determining the atomic occupancy and

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crystal structure for 5d transition metal nitrides, because of the similar neutron scattering lengths for Ta atom (0.6910×10^{-12} cm) and N atom (0.936×10^{-12} cm). The occupation of N atom also can be determined by neutron powder diffraction, so NPD is an effective way to confirm the crystal structure for the compounds consisting of heavy transition metals and light elements like N and H, compared to the x-ray powder diffraction. In this work, we employ neutron powder diffraction (NPD) to determine crystal structure and atomic occupation and *in-situ* high-pressure synchrotron x-ray diffraction to investigate the structural response of tantalum nitrides to pressure.

2. Experimental details

The high *P*–*T* synthesized experiments were performed using a DS 6×14 MN cubic press installed at Sichuan University, China. Tantalum nitride (Alfa Aesar No. 13093 Purity 99.5%) was used as the starting material. WC-type TaN bulk alloy was synthesized from hexagonal CoSn-type TaN by phase transformation sintering method under high pressure and high temperature (HPHT). After polishing the surface, the Vickers hardness was measured using a diamond indenter (FV-700B, Future-Tech, Japan). We conducted *in situ* high-pressure synchrotron x-ray diffraction on WC-type TaN in order to determine the well-constrained pressure dependence of its elastic modulus. The XRD measurements were made on the power of bulk sample in a diamond anvil cell up to 41 GPa. The *in situ* high-pressure synchrotron x-ray diffraction measurements were performed at the 4W2 beam line of the Beijing Synchrotron Radiation Facility (BSRF, China). High pressure was generated using a symmetric-type diamond anvil cell (DAC) with 300-μm culets.[20] A Si (111) monochromator was used to tune the synchrotron source with a wavelength of 0.6199 Å. The incident x-ray beam was focused to approximately 26 μm×8 μm full width at half maximum (FWHM) spot by a pair of Kirkpatrick–Baez mirrors. The two-dimensional diffraction patterns were recorded by a Mar345 image plate detector and analyzed with the program Fit2D.[21] The NPD experiments were carried out at room temperature using a neutron powder diffractometer at the Institute of Nuclear Physics and Chemistry, China. NPD data were collected at a wavelength of $\lambda = 1.59$ Å over the range of $2\theta = 20°$–$140°$ with a step of 0.1°/s. The counting time was 10 h with a neutron flux of 3×10^5 n·cm^{-2}·s^{-1} at the sample position. The obtained NPD patterns were refined by using FULLPROF SUITE ver.1.10 rietveld refinement software. The atomic ratios were roughly determined by an improved energy dispersive x-ray spectroscopy (EDX) method (Oxford Instruments, INCA E250), and then used for further NPD refinements. Before EDX quantitative analyses, the well-polished samples and the EDX standard samples were uniformly coated with an osmium layer (5 nm in thick) in an osmium coater (Neoc-STB, Meiwafosis Co., Ltd). The EDX method used in this work can effectively improve the accuracy of the quantification of light and heavy elements (such as Ta and N), and the accuracy of the quantification was evaluated to be less than 0.5%.[22,23] EDX analyses are consistent with the NPD results about the ratio of Ta atom and N atom.

3. Results and discussions

The well-synthesized samples are cylinder-shaped chunks with a diameter of about 8 mm and thickness of about 8 mm (the inset of Fig. 1(b)). Figure 1(a) shows XRD patterns of the starting material and sample synthesized at 5 GPa and 1873 K, it is clearly seen that the WC-type TaN can be obtained by treating CoSn-type TaN at 5 GPa and 1873 K. But there are XRD peaks of Ta_5N_6 existing in the patterns besides peaks which belong to CoSn-type and WC-type TaN. It means that there is a little Ta_5N_6 in the starting material and this may be a result that the synthesis method of CoSn-type TaN is used at present, in which impurities are apt to be introduced. In addition, Ta_5N_6 is stable under this condition during the synthesis of WC-type TaN from

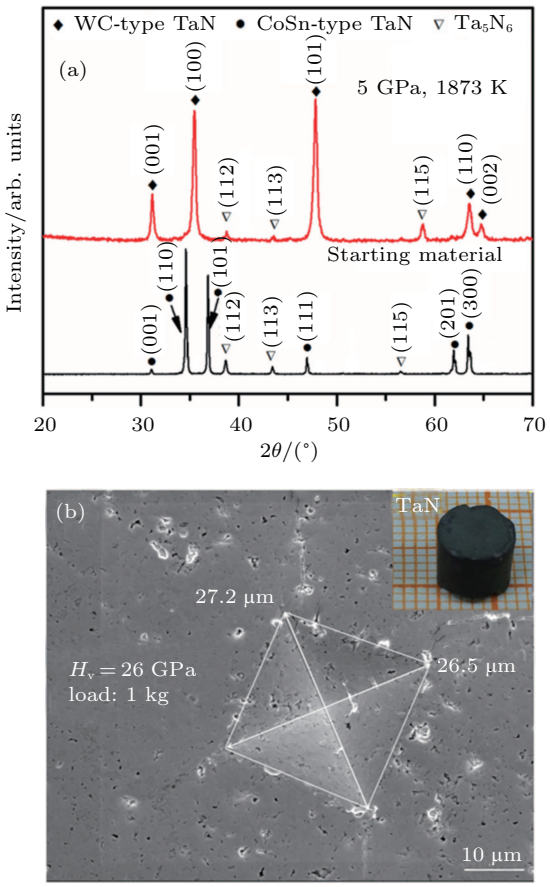


Fig. 1. (color online) (a) XRD pattern of starting material and WC-type TaN compacts synthesized under high pressure and temperature, (b) a typical FE-SEM image of Vickers indentation produced by a diamond pyramidal indenter under a load of 1 kg, inset: an optical photograph of TaN compact.

its XRD peaks. Hardness measurements were performed on these compacts by means of a Vickers indentation method using a pyramidal diamond indenter. So the Vickers hardness was measured under a loading force of 1 kg, the hardness of WC-type TaN compact is 26(2) GPa.

Figure 2 illustrates the refined NPD patterns for WC-type TaN and Ta_5N_6. WC-type TaN (space group *P*-6*m*2) is found to be the main phase with relative intensity of NPD peaks. Table 1 lists the refined structural data of the two nitrides with space group *P*-6*m*2 and $P6_3$-*mcm*. The refined lattice parameter $a = 2.929$ Å, $c = 2.880$ Å for WC-type TaN is not consistent with the lattice constants, $a = 2.933$ Å, $c = 2.883$ Å reported by Hitoshi *et al.*[15] NPD refinements show that the ratio of Ta atom and N atom is 1:0.927 in the WC-type TaN and 1:0.95 in the Ta_5N_6. Neutron scattering lengths are *b* (Ta) = 0.6910×10^{-12} cm and *b* (N) = 0.936×10^{-12} cm.[24] Because of the neutron scattering lengths for Ta atom and N atom, the crystal structure of WC-type TaN can be confirmed precisely and viewed as alternate stacking of Ta and N layers along the *c* direction. Thus, different Ta layers along the *c* axis are connected by the covalent bonding between Ta atoms and N atoms.

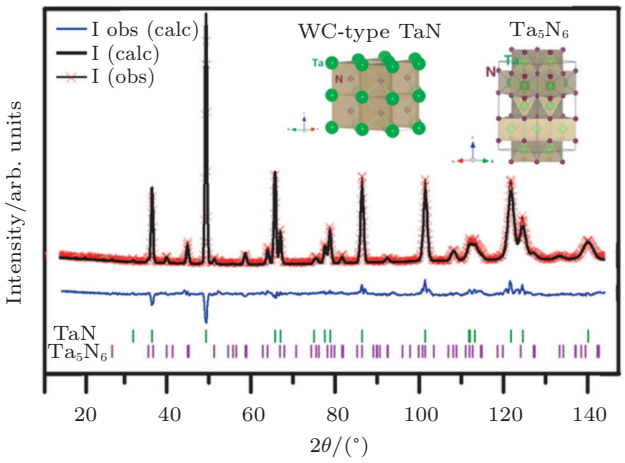


Fig. 2. (color online) Refined NPD pattern for WC-type TaN and Ta_5N_6, inset: structures of WC-type TaN and Ta_5N_6 determined by NPD structural data, green balls denote Ta atoms and red balls denote N atoms.

Table 1. Rietveld refined NPD structural data for the WC-type TaN and Ta_5N_6 for the preferred *P*-6*m*2 and $P6_3$-*mcm* hexagonal phase (a) WC-type TaN, lattice parameter $a = 2.929$ Å, $c = 2.880$ Å, (b) Ta_5N_6, lattice parameter $a = 5.196$ Å, $c = 10.390$ Å, Atomic position (*x*, *y*, and *z*) and site occupancy (occ.) also are given.

Phase	Atom	Wyckoff	*x*	*y*	*z*	occ.
WC-type TaN	Ta	1a	0	0	0	0.830
	N	1d	1/3	2/3	1/2	0.770
Ta_5N_6	Ta	4d	1/3	2/3	0	0.167
	Ta	6g	1/3	0	0.25	0.250
	N	12k	1/3	0	0.625	0.407

The compressible behaviors of the WC-type TaN and Ta_5N_6 under high pressure were investigated by *in situ* high-pressure synchrotron x-ray diffraction. The diffraction spectra of WC-type TaN and Ta_5N_6 are displayed in Fig. 3(a) from ambient pressure to more than 41 GPa. With the increased pressure, the diffraction peaks of WC-type TaN and Ta_5N_6 visibly shift to a high angle, which shows the compression behavior of WC-type TaN and Ta_5N_6. Under the testing pressures, no new diffraction peaks are detected from the curves, indicating that the structures of two phases are stable under high pressure. In Fig. 3(b), Rietveld refinement of the XRD patterns using the General Structure Analysis System GSAS software enabled the determination of the lattice parameters of WC-type TaN and Ta_5N_6.[25]

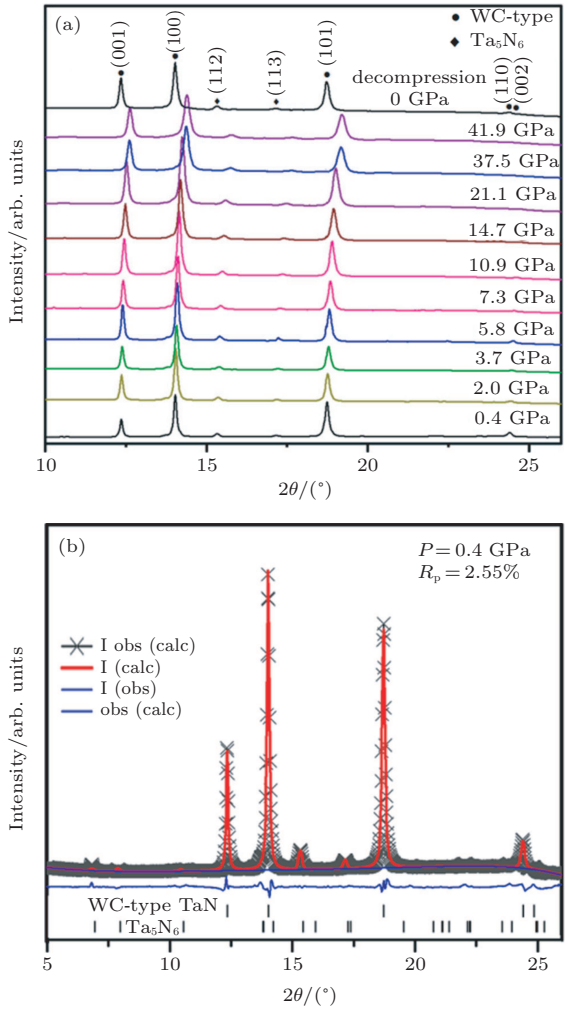


Fig. 3. (color online) (a) Selected x-ray diffraction patterns of tantalum nitrides at different pressure and the pattern collected on pressure release. (b) Rietveld refinement results of tantalum nitrides at 0.4 GPa.

The pressure-dependent volume measurements are shown in Fig. 4(a). The *P*–*V* data of WC-type TaN and Ta_5N_6 are fitted with a third-order Birch–Murnaghan equation of state,[26,27]

$$P = \frac{3}{2}B_0\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right] \times \left\{1 - \frac{3}{4}(B_0' - 4)\left[1 - \left(\frac{V}{V_0}\right)^{-2/3}\right]\right\}, \quad (1)$$

where B_0 and V_0 are the bulk modulus and united-cell volume in ambient condition, respectively, and B_0' is the pressure derivative of B_0. Fitting the results to a third-order Birch–Murnaghan equation with $B_0' = 4$ yields an ambient bulk modulus $B_0 = 369(2)$ GPa for WC-type TaN and $B_0 = 278(2)$ GPa. As can be seen in Fig.4(a), the bulk modulus of WC-type TaN is higher than that of the previous value (351(2) GPa) from the ref 15 and close to the latest value (378 GPa).[14] In addition, it can be seen that the compression of WC-type TaN is anisotropic, with the a-axis being more compressible than the c-axis from the Fig.4(b).

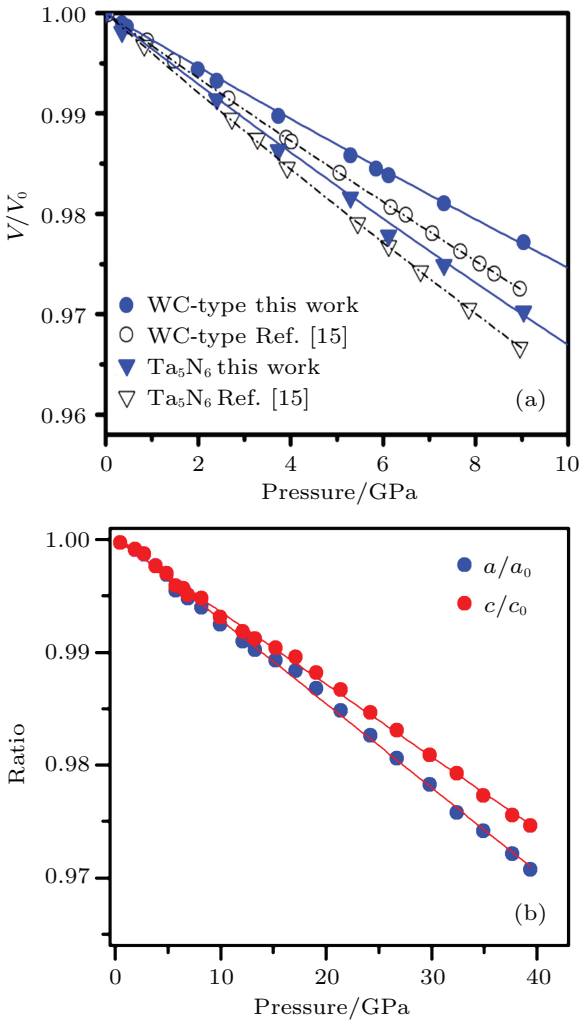


Fig. 4. (color online) (a) comparison of the high-pressure equations of state of WC-type TaN and Ta_5N_6, (b) the variations of lattice constants of WC-type TaN with pressure.

From *in-situ* high-pressure synchrotron x-ray diffraction Rietveld refinement data and the structure determined by NPD of WC-type TaN, the pressure dependence of distance of different atoms in WC-type TaN crystal is shown in Fig. 5. We find that the distance of adjacent Ta atoms along the c axis is not an obvious decrease with increase the pressure. In contrast, the distance of adjacent Ta atoms along a axis and b axis is easy to compress from the slope of the variations of lattice constants with pressure. Thus, the bonding along the c axis is dominated by covalent Ta–N bonds, which is less compressible from the distance of Ta and N atoms with increase the pressure. It is the result that the a axis of WC-type TaN crystal is more compressible than the c axis.

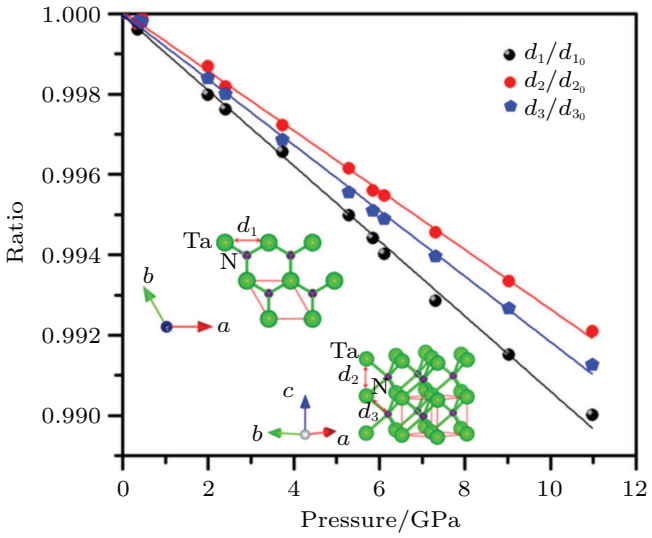


Fig. 5. (color online) The variations of the different atomic distance in WC-type TaN crystal.

4. Conclusions

In summary, crystal structure and atomic occupation of WC-type TaN have been re-determined by neutron power diffraction. Phase stability and compressibility of WC-type TaN and Ta_5N_6 have been studied at pressures up to 41 GPa using *in situ* high-pressure synchrotron x-ray diffraction in a diamond anvil cell. WC-type TaN and Ta_5N_6 are found to be stable with the pressure below 41 GPa. The bulk modulus of WC-type TaN and Ta_5N_6 derived from the P–V measurement data are 369(2) GPa and 287(3) GPa, experimental observations demonstrate that the a axis is more compressible than the c axis in the WC-type TaN crystal. This anisotropy can be attributed to the Ta–N covalent bond strengthening between the layered stacking of Ta and N atoms along the c axis. In addition, experimental observations also demonstrate the covalent bond Ta–N and high valence electron density of Ta atoms play an important role in the incompressibility of WC-type TaN.

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