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High-pressure study of low-compressibility Ta_2N

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Abstract

Room temperature synchrotron x-ray diffraction experiments were performed on nanocrystal Ta_2N in a diamond anvil cell to a pressure of 55.48 GPa. This nitride is a well-known kind of high-hardness material, and it is found to be highly incompressible. The structure is stable with no phase transitions observed in this pressure range. The zero-pressure bulk modulus and its pressure derivative at ambient pressure are $B_0 = 360 \pm 3$ GPa, $B_0' = 4$, and in room conditions, the a and c parameters are 3.054 Å, 4.996 Å, respectively. The bulk modulus of Ta_2N is greater than those of TaC, ε-TaN, Cr_2N and MoN. The differences in bulk moduli might be due to the differences in structure and the cohesive energy among these phases.

1. Introduction

Transition metal nitrides have unique properties, such as good chemical stability, high strength, high hardness, high melting point, low electrical resistivity and high thermal conductivity, which have aroused broad interest [1, 2]. As an important candidate among these interstitial compounds, tantalum nitride has been found to be a promising material for many applications such as in diffusion barriers, wear and corrosion resistance, high-speed thermal printing heads, as well as precise and stable resistors used in silicon-based integrated circuits [3–6]. In particular, Papaconstantopoulos *et al* [7] theoretically predicted that cubic TaN has high superconducting critical temperature and Fu *et al* [8] synthesized a new nanocomposite exhibiting a zero-temperature coefficient of resistivity, which is composed of tantalum nitride and copper nanoparticles. Despite other bulk mechanical properties have been determined, very few studies of the compressibility of such high-hardness materials have been carried out. In recent years, high-pressure studies on nanocrystal materials have aroused great enthusiasm because the size of the nanoparticles has a significant effect on the phase transition and the

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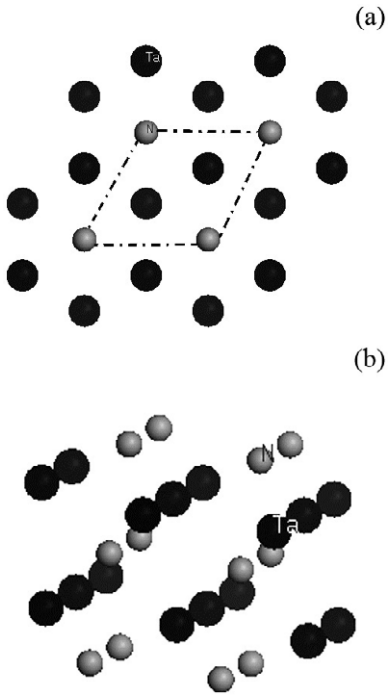

Figure 1. The structure of hexagonal Ta_2N: (a) view of the (0001) plane and (b) perspective view. The unit cell is indicated by the dot–dashed lines. The small spheres represent the N atoms and the large spheres represent the tantalum atoms.

compressibility. Generally, the bulk modulus and phase transition pressure increase with decreasing particle size [9, 10]. In contrast, it is observed that the nanocrystal materials display a weakened transition pressure due to the particle size being below 15 nm and the volumetric expansion [11–13]. Nevertheless, there are also nanocrystals (e.g. of GaAs and SnO_2) [14, 15] whose phase transition pressure is constant and independent of the crystallite size. Therefore, we expect to be able to explore some potentially novel mechanisms for the pressure-induced first-order solid–solid phase transformations and the bulk modulus variations of nanocrystals through high-pressure studies on Ta_2N nanocrystals.

Here we report studies of high-pressure behavior of nanocrystal Ta_2N in a diamond anvil cell using an *in situ* energy-dispersive synchrotron radiation technique. The sizes of the Ta_2N nanocrystals are about 5–10 nm. The structure of Ta_2N is stable, with no phase transitions observed in this pressure range. The bulk modulus and its pressure derivative have been estimated by fitting a third-order Birch–Murnaghan equation of state to the unit cell volume versus pressure data. The results show that the zero-pressure bulk modulus and its pressure derivative at ambient pressure are $B_0 = 360 \pm 3$ GPa, $B_0' = 4$.

2. Experimental details

The Ta_2N nanocrystals studied here were previously obtained by the dc arc plasma method through the reaction of metal tantalum (Ta) with a mixture gas of nitrogen (N_2) and ammonia (NH_3) [16]. The sample used here has an average diameter of 5–10 nm. The sample

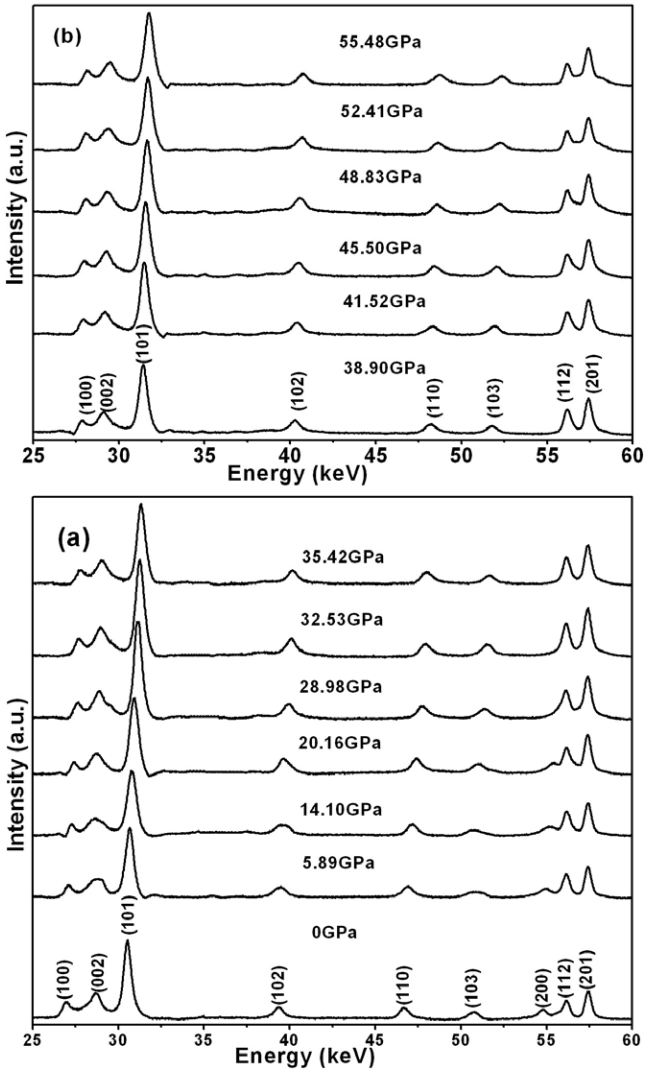

Figure 2. X-ray diffraction patterns of Ta_2N nanocrystals.

composition and phase purity were confirmed using corresponding electron diffraction pattern analysis and powder x-ray diffraction. The pressure was generated in a diamond anvil cell with the diamonds had a culet size of 300 μm. The samples, with the 16:3:1 methanol:ethanol:water mixture pressure-transmitting medium, were loaded into a 100 μm hole drilled in a T301 stainless steel gasket. The pressure was determined by measuring the wavelength shift of the ruby R_1 and R_2 luminescence lines and applying the non-linear pressure scale of Mao *et al* [17].

The *in situ* high-pressure x-ray diffraction (XRD) measurement was performed with an energy-dispersive synchrotron x-ray source at beamline X17C of the National Synchrotron Light Source, Brookhaven National Laboratory. At X17C the detector was positioned at $2\theta = 11.0025°$.

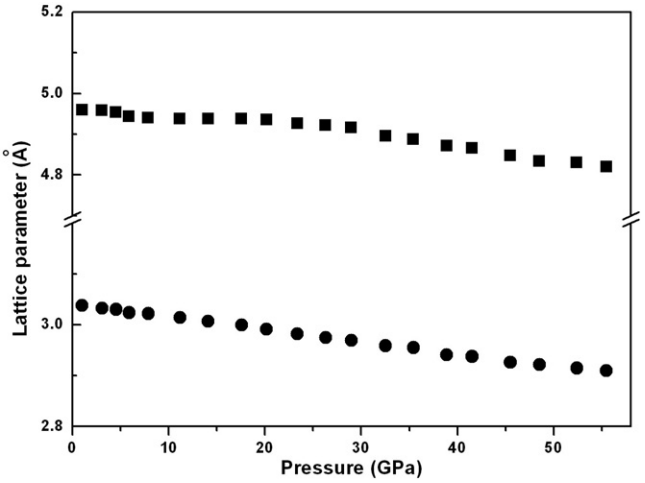

Figure 3. The a and c lattice parameters as a function of pressure for Ta_2N. The spheres represent a and the squares represent c.

3. Results and discussion

The Ta_2N at ambient pressure has a crystal structure (space group $P63mmc$ (194)) with three atoms in the unit cell [18]. The geometry of hexagonal Ta_2N is presented in figure 1.

The x-ray diffraction patterns of Ta_2N nanocrystals are shown in figure 2 for the range of 0–55.48 GPa. At ambient conditions, all the diffraction peaks can be indexed to a pure h-Ta_2N crystal with lattice constants of $a = 3.054$ Å and $c = 4.996$ Å. This is consistent with the reported value for Ta_2N ($a = 3.044$ Å, $c = 4.914$ Å, JCPDS card No. 26-0985). There are nine clear peaks at ambient conditions, which can be indexed with the (100), (002), (101), (102), (110), (103) (200), (110) and (201) crystal planes of h-Ta_2N. No extra peaks appear in the XRD patterns up to a stress of 55.48 GPa, which is the highest pressure reached in this study. It is suggested that there are no phase transitions in this pressure range. To our knowledge, this is the first time that the effect of pressure on Ta_2N nanocrystals has been studied experimentally.

The pressure dependences of the a and c lattice parameters and the d-spacings of Ta_2N from 0 to 55.48 GPa are summarized in figures 3 and 4. A continuous decrease in the values of the d-spacings has been observed with increase in pressure (figure 4). The lattice parameters and the d-spacings do not show any anomaly that might be associated with a structural phase transition. Figure 5 shows the pressure–volume data for Ta_2N nanocrystals. The data were fitted with a third-order Birch–Murnaghan equation of state:

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

where B_0 and B_0' are the isothermal bulk modulus and its pressure derivative at ambient temperature, respectively. In order to facilitate the comparison of the B_0 values, we have followed the standard procedure of setting $B_0' = 4$. The fitting results for Ta_2N nanocrystals give the bulk modulus $B_0 = 360 \pm 3$ GPa. This is significantly smaller than the value $B_0 = 378$ GPa for tantalum nitride observed from the previous theoretical results [19, 20]. As a comparison, elemental Ta has a bulk modulus of $B_0 = 174$ GPa with $B_0' = 4$ [21]. The Ta_2N nanocrystals are less compressible than the pure metal, due to the increasing number of valence d electrons and the presence of electrons in the core [22]. The bulk modulus of Ta_2N is greater than the 345 ± 9 GPa for TaC, 288 ± 6 GPa for ε-TaN, 275 ± 23 GPa for Cr_2N and

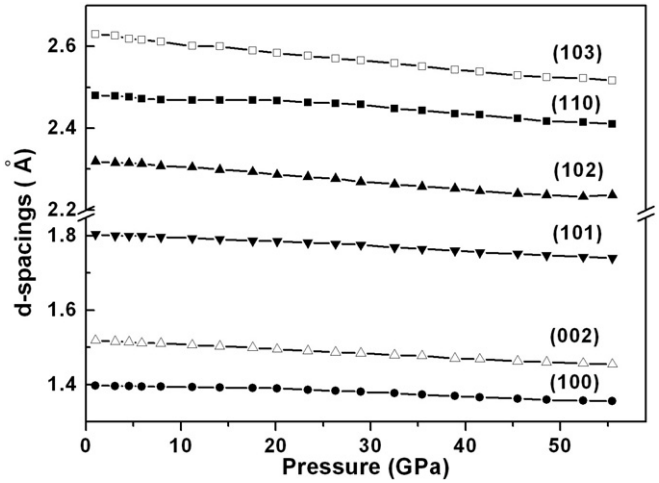

Figure 4. Lattice plane spacings as functions of pressure for Ta_2N. Miller indices hkl are given.

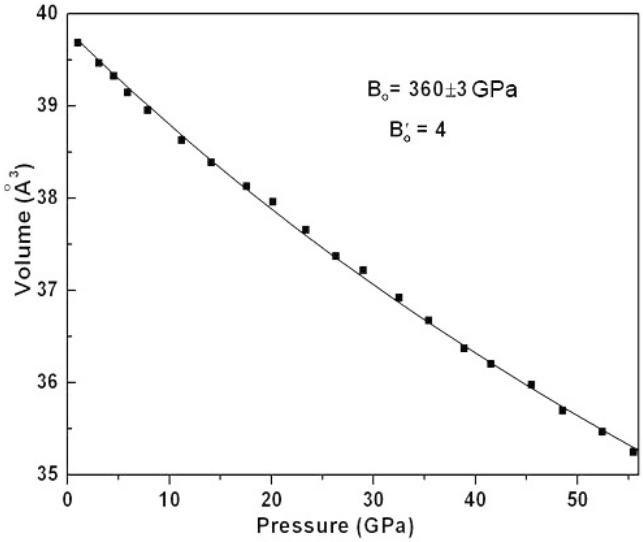

Figure 5. Pressure–volume relation for Ta_2N nanocrystals; the line represents the fit to the third-order Birch–Murnaghan equation of state.

345 ± 9 GPa for MoN [23–25]. The differences in bulk modulus might be due to the differences in structure and cohesive energy among these nitrides.

4. Conclusions

In conclusion, we have measured a remarkably high value of the bulk modulus for the well-known high-hardness material Ta_2N ($B_0 = 360 \pm 3$ GPa and $B_0' = 4$). This is the first time that the effect of pressure on Ta_2N nanocrystals has been studied experimentally. The structure of Ta_2N is stable with no phase transitions observed in this pressure range. The results are compared with ones for other nitrides (e.g. ε-TaN, Cr_2N and MoN); it is found that the bulk

modulus of Ta_2N is the highest among the various values. These results confirm that Ta_2N is a high-hardness material, and it is found to be highly incompressible.

Acknowledgments

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