

A Study of the Structural Stability of TiC, TiN and TiO in the Pressure Range up to 65 GPa Using Synchrotron Radiation*

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The titanium compounds TiC, TiN and TiO are cubic with the NaCl type structure (space group $Fm\bar{3}m$). The lattice constant decreases monotonically along the series TiC, TiN and TiO, together with a decreasing radius of the non-metal atom. These compounds have a wide range of non-stoichiometry. TiC and TiN have mainly vacancies on the carbon and nitrogen sublattices, respectively. TiO has vacancies on the titanium as well as the oxygen sublattices. The vacancies are arranged in a short-range order that upon annealing can result in a long-range order of the occupied and vacant sites in the metal and non-metal sublattices. In the case of TiO this results in a monoclinic unit cell. The non-stoichiometry of the compounds makes the cubic unit cell parameter dependent on the composition x , corresponding to the chemical formulae TiC_x , TiN_x and TiO_x .

Structural phase transformations in TiC, TiN and TiO could possibly occur at high pressure because of the non-stoichiometric nature of these compounds. The NaCl structure could then possibly transform to the CsCl structure, in which case the coordination number would increase from six to eight. This is in agreement with the general rule that the coordination number increases with pressure. The present work was undertaken in order to investigate possible structural phase transformations in TiC, TiN and TiO in the pressure range up to 65 GPa (= 650 kbar).

Experimental

X-Ray powder diffraction spectra were recorded at HASY-LAB-DESY, Hamburg, FRG, using synchrotron radiation and the white-beam energy-dispersive method. Experimental details have been published elsewhere.¹ The electron energy of the storage ring DORIS II was 3.7 GeV in a run

dedicated to synchrotron radiation work. High pressure was achieved in a diamond anvil cell, where the sample and a small ruby chip was inclosed in small hole (diameter 0.1 mm) in an Inconel gasket. A 4:1 methanol:ethanol mixture was used as the pressure transmitting medium. The pressure was determined from the wavelength shift of the red ruby line using the nonlinear pressure scale of Mao *et al.*²

Diffraction lines from the gasket were avoided by reducing the incident beam cross-section to 0.06 mm × 0.06 mm using two pairs of crossed slits. The lattice constant at atmospheric pressure was determined from a zero-pressure spectrum with the sample situated in the diamond anvil cell. The Bragg angle associated with the diffraction spectrum was found from another zero-spectrum, where the sample was replaced by a NaCl powder with a known lattice constant. All experiments were performed at room temperature.

Results and discussion

The unit cell constants were refined by a least-squares method using nine diffraction lines, recorded in an energy range from 20 to 57 keV for a Bragg angle of 7.2°. All diffraction spectra of TiC, TiN and TiO could be indexed assuming the NaCl type structure. Thus, contrary to expectations, no structural phase transformations occur in the observed pressure range. In the case of TiN a slight distortion of the cubic unit cell was observed for pressures above about 20 GPa. This is illustrated in Fig. 1, where we have plotted the ratio between the observed spacings of the (111) planes and the (200) planes as a function of pressure. For a cubic lattice the theoretical value is 1.155. As seen in Fig. 1 the observed value rises to about 1.16 above 20 GPa. The distortion is possibly a preparatory stage for a phase transformation at a still higher pressure.

The variation of the unit-cell volume V , with pressure, P , can be described by the Murnaghan equation of state,³

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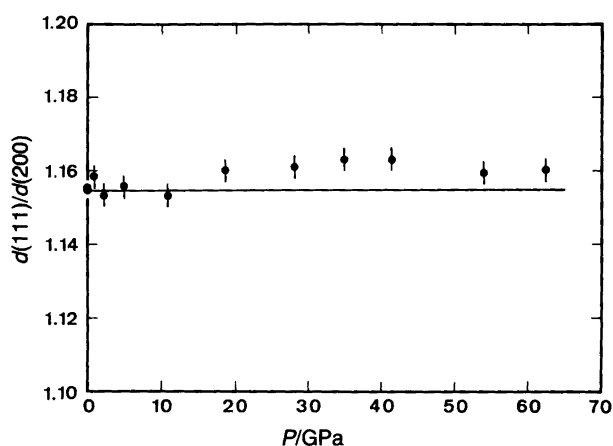


Fig. 1. Ratio between the spacings of the (111) planes and the (200) planes for TiN as a function of pressure. The horizontal line indicates the theoretical value 1.155 for a cubic lattice.

$$P = (B_0/B_0') [(V_0/V)^{B_0'} - 1] \quad (1)$$

eqn. (1), where V_0 is the volume at zero pressure, B_0 the isothermal bulk modulus and B_0' its pressure derivative, evaluated at zero pressure. Table 1 lists the B_0 and B_0' values resulting from least-squares fits of the Murnaghan equation of state to the experimental pressure–volume data. Also included in Table 1 are the lattice constants, a_0 , at atmospheric pressure, determined as described above. They agree within the experimental errors with the corresponding values given by Wyckoff:⁴ 4.319, 4.235 and 4.177 Å for TiC, TiN and TiO, respectively.

Concerning the pressure–volume relation, TiO is the most well-behaved sample of the three compounds. As seen in Fig. 2c the Murnaghan equation of state describes the experimental data very well in the whole pressure range. Moreover, the pressure derivative of the bulk modulus is close to 4, which is a normal value for most solids. Thus we have some confidence in the resulting value of 250 GPa for the bulk modulus, although it is 30% larger than the value of 182 GPa given by Taylor and Doyle.⁵ It should also be noted that the pressure range in our case is ten times larger than in the previous determination.

The pressure–volume data for TiC and TiN are more scattered, and it has not been possible to fit to a single equation of state in the entire pressure range. Thus the B_0

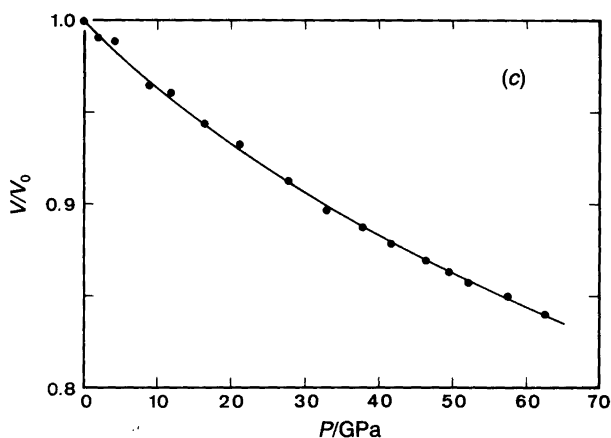
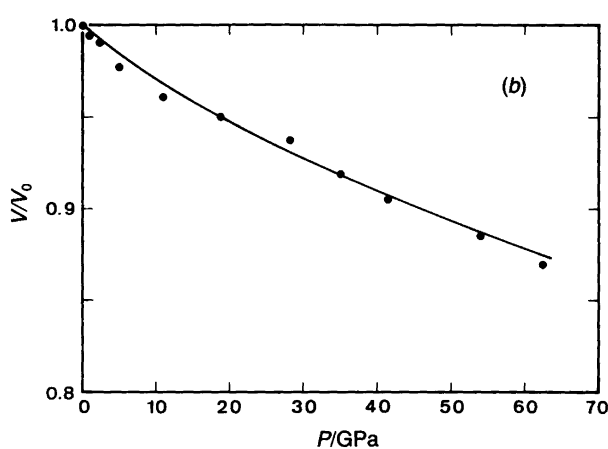
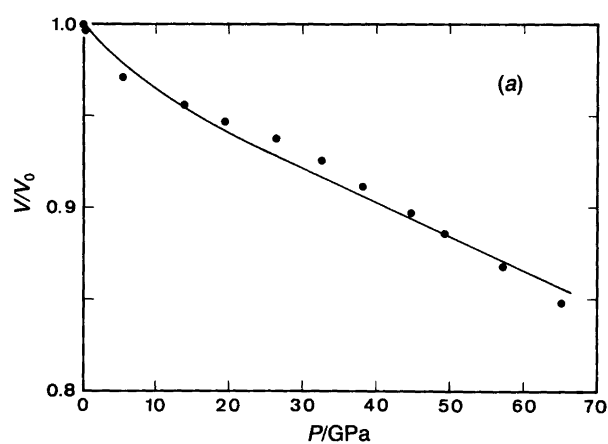


Fig. 2. Relative volumes as a functions of pressure. The full curves have been calculated from the equation of state using the data from Table 1. (a) TiC, (b) TiN, (c) TiO.

Table 1. Lattice constant, a_0 , bulk modulus, B_0 , and its pressure derivative, B_0' , evaluated at zero pressure. The uncertainties, given in parentheses, are the standard errors of the least-squares fits to the experimental data.

Compound	$a_0/\text{Å}$	B_0/GPa	B_0'
TiC	4.328(9)	220(30)	12(4)
TiN	4.237(2)	300(40)	7(3)
TiO	4.181(4)	250(10)	4.0(4)

and B_0' values given in Table 1 have been obtained in the pressure ranges up to 25 GPa for TiC and up to 40 GPa for TiN. Also the large B_0' values are suspect. The irregular behaviour might be related to rearrangements of the vacancies in the samples at high pressure. The bulk moduli are in good agreement with the few published values available. For TiC Drickamer *et al.*⁶ quote 220 GPa and Bridgman⁷ quotes 208 GPa. From elastic constants given by

Toth⁸ one can calculate 240 GPa. For TiN Bridgman⁷ has measured a bulk modulus of 295 GPa.

In conclusion, we have found that TiC, TiN and TiO retain their NaCl type structure in the pressure range up to 65 GPa. Bulk moduli are in good agreement with the few published values for TiC and TiN, whereas our value for TiO is 30 % larger than a previous determination.

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