

Experimental report – ID24 (CH-2851)

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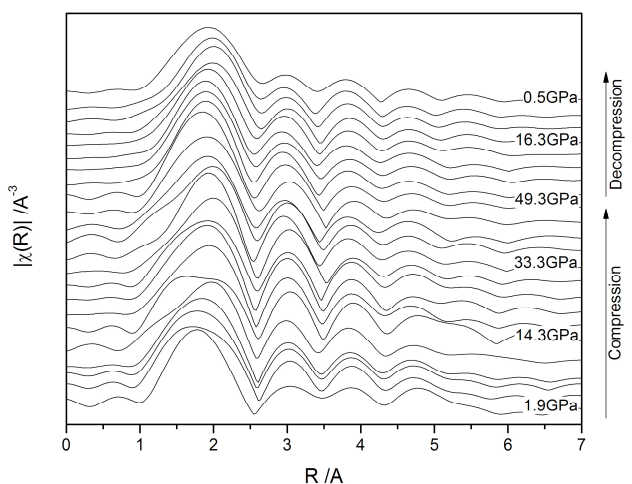
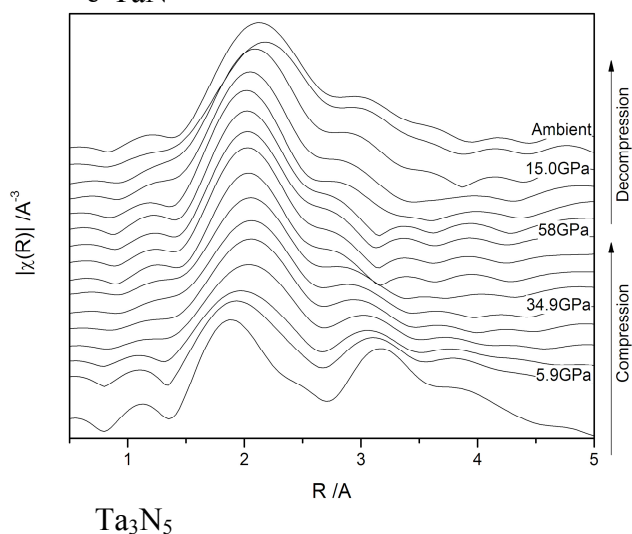
Introduction

Transition metal nitrides and oxynitrides are important refractory ceramics with high hardness and superconductive properties. Most of the nitride phases are observed only as mononitrides, although some of the higher oxidation state nitrides are accessible via chemical or high-pressure synthesis routes¹. The Ta_3N_5 phase is well characterised at ambient conditions, and is predicted to undergo a phase transition above 9GPa². TaON is similarly expected to undergo a phase transition at 30GPa³. ϵ -TaN does not undergo a phase transition, but exhibits an interesting crossing over of two Raman bands as pressure is increased⁴. These Ta-(O)-N systems have been studied by micro-X-ray absorption spectroscopy (XAS) at ID24 during compression and decompression in a DAC, and the initial results are described here.

One possible route to these new Ta-(O)-N phases is to use amorphous precursors of an appropriate stoichiometry, and apply high pressures and temperatures to elicit a reaction. The precursors are synthesised initially by the ammonolysis of a transition metal amide, followed by the pyrolysis of the intermediate product at 350-400°C under a dry flowing N_2/NH_3 mixture⁵. Raman spectroscopy and X-ray diffraction show no notable features, and support the notion that the final products are amorphous. The XAS spectrum of this compound is shown here.

Results

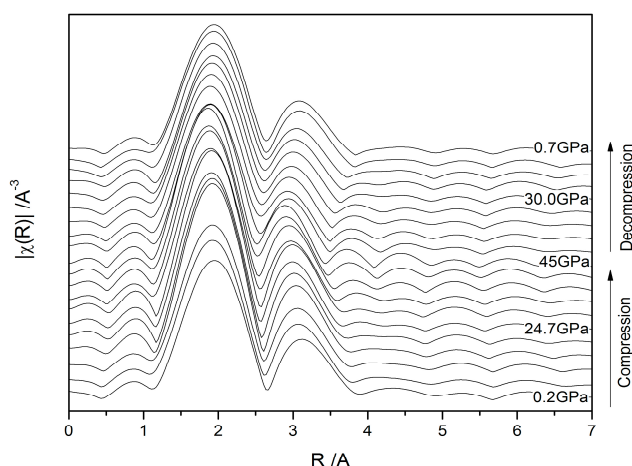
ϵ -TaN



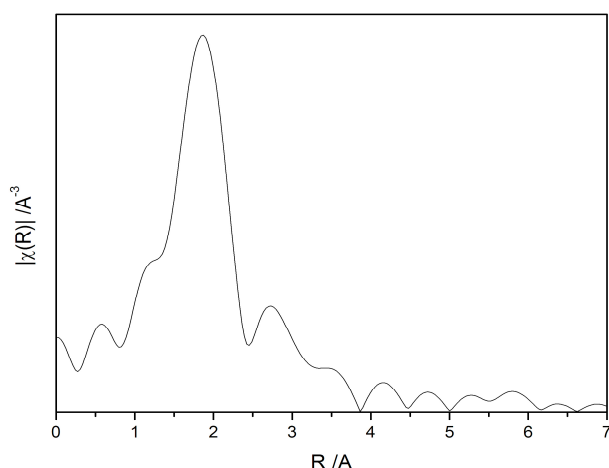
The Fourier transformed EXAFS region has been modelled, and initial analysis shows that no significant change occurring in the first shell until above 50GPa, where it decreases upon compression. This distance represents the Ta—N bond. Upon decompression, this distance increases to a value greater than that observed at ambient pressure prior to compression. The second shell (Ta-Ta distance) exhibits a more pronounced decrease upon compression, and increase upon decompression, and it is believed that the Ta coordination increases at higher pressures, and is an irreversible change.

The compression and decompression of Ta_3N_5 suggests that the overall structure remains the same throughout. The slight variations observed here are more likely due to artefacts from the diamond glitches that were a problem when recording this data. No phase transition is obvious, and harsher conditions such as elevated temperatures may be needed to induce the predicted change.

TaON



Ta_xN_y



The spectra illustrating the compression and decompression of TaON shows a slight decrease in the first shell distance upon compression, followed by a slight increase upon decompression. The second shell follows a similar pattern, although the variation is more pronounced. This change appears at first sight be reversible, unlike that for TaN. Again, no phase transition is immediately obvious, and harsher conditions may be necessary for this transition to take place.

The ambient spectrum for the amorphous/nanocrystalline Ta_xN_y sample shows that there is a strong first shell peak corresponding to the Ta—N bonds, but beyond that there is no defined second shell, confirming that this compound has no long-range order.

Summary

We have investigated the effect on the local structure and coordination of compressing and decompressing samples of ϵ -TaN, Ta₃N₅ and TaON, and have initial XAS data on a novel amorphous Ta_xN_y precursor. An initial

analysis of the ϵ -TaN data supports previous Raman and X-ray diffraction data suggesting a subtle change in the local structure of the material upon the application of pressure. The Ta₃N₅ and TaON data show no obvious changes, and further studies such as a combined high-pressure, high-temperature approach will be needed to determine the synthesis and stability of the predicted phases.

¹ G Brauer and JR Weidlein, *Angew. Chem. Int. Ed.*, 1965, **4**, 241; A Zerr *et al*, *Nat. Mat.*, 2003, **2**, 185

² P Kroll *et al*, *Angew. Chem. Int. Ed.*, 2005, **44**, 4249

³ JE Lowther, *Phys. Rev. B*, 2006, **73**, 134110

⁴ E Soignard *et al*, *Phys. Rev. B*, 2007, **75**, 014104

⁵ AW Jackson, O Shebanova, AL Hector, PF McMillan, *J. Solid State Chem.*, 2006, **179**, 1383