High-Pressure Annealing of a Prestructured Nanocrystalline Precursor to Obtain Tetragonal and Orthorhombic Polymorphs of Hf_3N_4

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ABSTRACT

Transition metal nitrides containing metal ions in high oxidation states are a significant goal for the discovery of new families of semiconducting materials. Most metal nitride compounds prepared at high temperature and high pressure from the elements have metallic bonding. However amorphous or nanocrystalline compounds can be prepared via metal-organic chemistry routes giving rise to precursors with a high nitrogen:metal ratio. Using X-ray diffraction in parallel with high pressure laser heating in the diamond anvil cell this work highlights the possibility of retaining the composition and structure of a metastable nanocrystalline precursor under high pressure-temperature conditions. Specifically, a nanocrystalline Hf_3N_4 with a tetragonal defect-fluorite structure can be crystallized under high-P,T conditions. Increasing the pressure and temperature of crystallization leads to the formation of a fully recoverable orthorhombic (defect cottunite-structured) polymorph. This approach identifies a novel class of pathways to the synthesis of new crystalline nitrogen-rich transition metal nitrides.

INTRODUCTION

Solid state compounds with transition metals in high oxidation states are often insulators or wide band gap semiconductors, e.g. TiO_2 and ZrO_2. The corresponding nitrides do not typically achieve maximum oxidation states and are dominated by metallic bonding. This is due to the highly exothermic formation enthalpy of the lower metal nitrides allied with the thermodynamic stability of gaseous nitrogen. Higher nitrides such as Ti_3N_4 should be stable[1] and could be accessed if a suitable synthesis route is found to achieve them. Lower band gaps are expected relative to the oxides, giving rise to semiconducting and photocatalytic properties, as well as highly colored compounds that can be used as pigments e.g. Ta_3N_5.[2] Recent high pressure and temperature elemental combination reactions in laser heated diamond anvil cells (LH-DAC) have led to new phases such as PtN_2, OsN_2 and Hf_3N_4.[1] However, most of these reactions at high pressure have only led to surface conversion or mixed phases and consequently low yields. Alternatively, synthesis routes involving metal-organic chemistry such as ammonolysis of metal amide complexes can lead to amorphous or nanocrystalline solids with a very high N:metal ratio.[3] Here we have shown that one such material can provide an ideal precursor for high-P,T synthesis experiments and that the precursor structure plays a key role in directing the polymorphism of the products.

EXPERIMENT

The precursor was nanocrystalline Hf_3N_4 prepared by ammonolysis of the tetraalkylamide complex $Hf(NEtMe)_4$.[7] Its diffraction pattern showed only a broad, diffuse signal indicative of an amorphous or nanocrystalline material. Based on our structural solution for the phase that crystallized at moderate P and T (see later) we analysed the local structure of the nanocrystalline starting compound that was thought previously to be based on a rocksalt (NaCl) arrangement of ions. Fitting the pair distribution function (PDF) with data collected at ID15B and diffraction data collected at SNBL against a series of models led to the conclusion that the same defective fluorite structure found for the crystalline polymorph is also the best description of the structure of the nanocrystalline material (Fig. 1). That result changes our understanding of local structural arrangements in nanocrystalline or amorphous materials produced from chemical synthesis experiments for heavy metal cations such as Hf^{4+} or Zr^{4+}, compared with lighter ions such as Ti^{4+} that do exhibit a rocksalt like arrangement.[3]

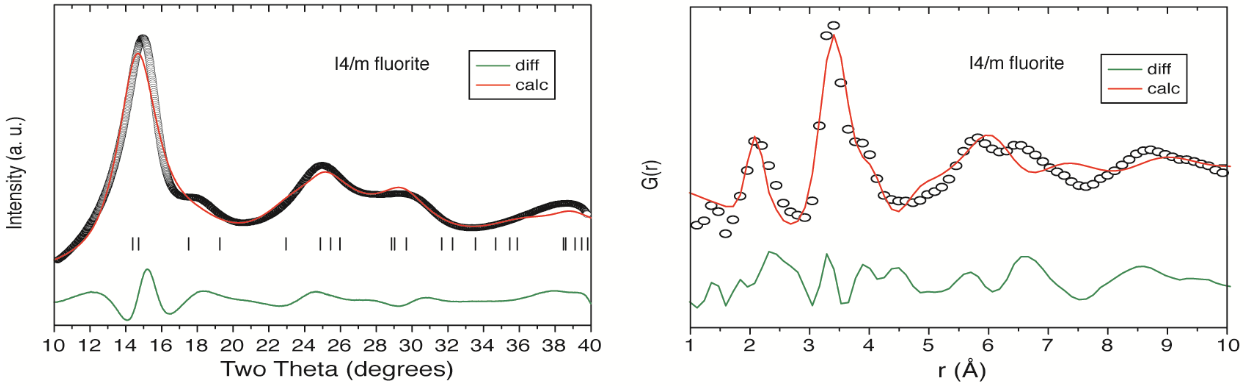

Figure 1. Rietveld (SNBL, $\lambda = 0.69775$ Å, left, $R_{wp} = 9.5\%$, $R_p = 8.0\%$) and PDF (ID15B $\lambda = 0.13788$ Å, right, $R_p = 32.0\%$) fits to the diffraction data collected with nanocrystalline Hf_3N_4. Both data sets identify a tetragonally distorted fluorite cell confirming that the structure of the precursor is retained at elevated pressure and temperatures (12 GPa and 1500 K).

High pressure synthesis used in situ X-ray diffraction and the LH-DAC facilities at beamline ID27 at ESRF to follow the progress of transformations of the nanocrystalline precursor and identify the products. The samples were loaded into DACs inside a glove box and charged with a nitrogen pressure transmitting medium under rigorously inert conditions. Upon heating to 1500 K at 11 GPa a series of sharp crystalline peaks was observed to appear. We determined that a tetragonally distorted version of an anion-deficient fluorite structure had formed (space group I4/m), with all the metal sites filled with Hf^{4+} cations, and the anion sites occupied by N^{3-} and vacancies (Fig. 1).[7] Increasing the pressure to 20 GPa and carrying out extended heating to 2000 K resulted in a new crystalline diffraction pattern that we identified as an orthorhombic cotunnite-type phase, containing 25% vacancies distributed along with N^{3-} ions on the anion sites (Fig. 2).[7]

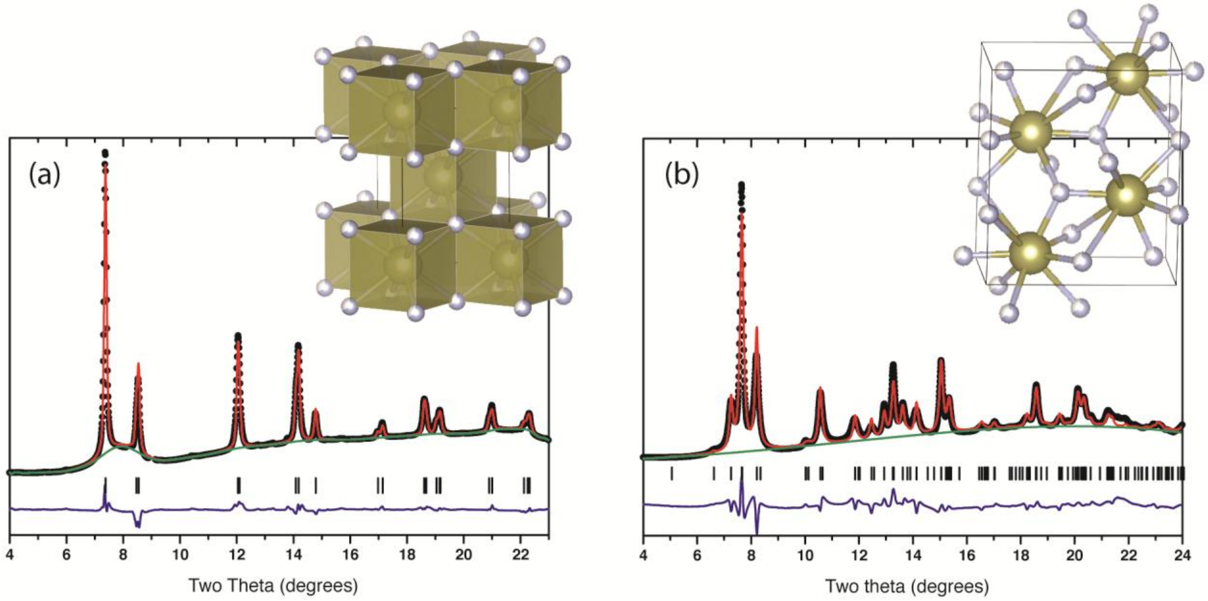

Figure 2. Fits to the XRD patterns of Hf_3N_4 at different conditions with the corresponding structural model (ID27, $\lambda = 0.37380$ Å). The data points are shown as black dots and the Rietveld fit as a red line. The refined background is shown in green and the difference plot in blue. (a) Diffraction pattern of Hf_3N_4 obtained at 12 GPa and 1500 K using a tetragonally distorted fluorite model ($R_{wp} = 2.2\%$ and $R_p = 2.0\%$). (b) Hf_3N_4 at 19 GPa after laser heating at 2000 K using a defect cottunite structure model ($R_{wp} = 4.2\%$ and $R_p = 2.9\%$).

Neither of these polymorphs have been described in previous high-P,T studies and we did not observe formation of the cubic Th_3N_4-structured Hf_3N_4 phase that is obtained by elemental combination under similar conditions, indicating that the metal nitride exhibits a rich structural polymorphism among stable and metastable phases at high P and high T conditions. We used our refined cell parameters to obtain compressibility (V(P)) data for the two new polymorphs. The defective fluorite structure was less resistant to compression (bulk modulus $K_o = 200$ GPa) than the corresponding tetragonal oxide (HfO_2)[5] or Th_3P_4-structured Hf_3N_4,[4] as expected due to the presence of vacancies on the anion sites. However the new dense cotunnite phase had a higher K_o value, indicating a greater resistance to mechanical stress.

CONCLUSIONS

We have demonstrated that a high density orthorhombic form of Hf_3N_4 can be recovered to ambient conditions, and this is likely also the case for the tetragonal form. These new polymorphs could now be produced in larger quantities for examination of their properties using large volume press or shock wave techniques. The general approach of combining chemical precursor synthesis with high-P,T techniques and synchrotron X-ray diffraction can be applied to other transition metal containing systems to lead to new families of high oxidation state nitride compounds.

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