High-pressure high-temperature synthesis of novel binary and ternary nitride phases of group 4 and 14 elements

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Abstract. Our recent experiments on high-pressure high-temperature synthesis of novel ternary nitrides of group 4 and 14 elements are presented. Dense carbon nitride imide, $C_2N_2(NH)$, was synthesized for the first time in a laser heated diamond anvil cell (LH-DAC) at pressures above 27 GPa and temperatures around 2000 K. Based on results of the electron diffraction-, EELS- and SIMS-measurements combined with theoretical calculations the structure of this new C-N-H phase was suggested to be of the defect-wurtzite type. Farther, macroscopic amounts of a new oxynitride of zirconium having cubic Th_3P_4-type structure, $c\text{-}Zr_{2.86}(N_{0.88}O_{0.12})_4$, were synthesized at high pressures and temperatures using a multi-anvil apparatus. Earlier this structure was observed for binary nitrides of zirconium(IV) and hafnium(IV) synthesized in microscopic amounts in a LH-DAC. The lattice parameter of $c\text{-}Zr_{2.86}(N_{0.88}O_{0.12})_4$ was found to be $a_0 = 6.7549(1)$ Å which is slightly larger than that of $c\text{-}Zr_3N_4$. Isotropic bulk and shear moduli of $c\text{-}Zr_{2.86}(N_{0.88}O_{0.12})_4$ of $B_0 = 219$ GPa and $G_0 = 96$ GPa, respectively, were determined from the compression and nanoindentation measurements. The Vickers microhardness, $H_V(1)$, of the porous (about 30 vol. %) sample of $c\text{-}Zr_{2.86}(N_{0.88}O_{0.12})_4$ was measured to be 12 GPa, similar to that of single crystal δ-ZrN.

1. Introduction

The nitrides of group 4 and 14 elements, namely hexagonal α- and β-phases of Si_3N_4 and cubic mononitrides δ-TiN, ZrN and HfN, are well known industrial materials exhibiting such technologically useful properties as high hardness, wear and oxidation resistance, chemical and thermal stability. In 1999 a novel cubic phase of silicon nitride (γ-Si_3N_4) having spinel structure was synthesized at high pressures (>15 GPa) and temperatures (>2000 K) using a LH-DAC [1]. γ-Si_3N_4 was found to have high elastic moduli (B_0=290 GPa, G_0=148 GPa) and high hardness $H_V(0.5)$=30-43 GPa [2]. γ-Si_3N_4 is metastable at ambient pressure and on heating in air up to 1673 K [3].

In contrast to Si, Ge and Sn, there is still no evidence for existence of similar nitride phases for carbon. Since dense C_3N_4 polymorphs were predicted to have bulk moduli and hardness comparable to or even exceeding those of diamond [4, 5], a number of experimental efforts have been devoted to synthesize crystalline carbon nitride using different deposition and high-pressure high-temperature (HP-HT) techniques. However, the obtained CN_x phases were predominantly amorphous or nanocrystalline with structure and composition being not unambiguously determined [6]. Therefore, the existence of pure crystalline C_3N_4 polymorphs remains a matter of controversy within scientific community.

On the other hand the discovery of spinel nitrides of group 14 elements (Si, Ge, Sn) has entailed speculations on possible stability of analogous polymorphs for other tetravalent elements (i.e. Ti, Zr and Hf). This supposition, however, was not confirmed experimentally. Moreover, experiments with a LH-DAC have shown that at high pressures (>15 GPa) and high temperatures (>2500 K) Zr and Hf form another previously unknown family of nitrides having M_3N_4 stoichiometry (M=Zr or Hf) [7]. The novel nitrides (denoted hereafter c-M_3N_4) were found to have cubic Th_3P_4-type structure with cations 8-fold coordinated by nitrogen atoms. These were the first binary nitrides with cations exhibiting such a high coordination number. Preliminary measurements suggested for each of the compounds $B_0 \approx 250$ GPa (B'_0=4, fixed) indicating their high hardness. Subsequent theoretical studies predicted high elastic moduli [8-10] and hardness for c-M_3N_4 [9]. Thin films of c-Zr_3N_4 deposited by physical vapor deposition (PVD) technique were found to be significantly harder than δ-ZrN films and to exhibit extraordinary wear resistance upon machining of low carbon steel [11].

Here we report on the HP-HT synthesis of a well-crystallized carbon nitride imide, $C_2N_2(NH)$, in a LH-DAC from a single source precursor (dicyandiamide $C_2N_4H_4$) [12]. Single crystals of the new dense carbon nitride phase were recovered to ambient conditions and analyzed using TEM, EELS and SIMS. The carbon nitride imide has a defect-wurtzite structure (space group $Cmc2_1$) analogous to that of $Si_2N_2(NH)$ or Si_2N_2O. The bulk modulus of $C_2N_2(NH)$ was calculated to be 277 GPa.

We also present here the first HP-HT experiments on synthesis of macroscopic amounts (>1 mm^3) of oxygen-bearing cubic zirconium(IV) nitride, c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ [13]. The obtained material was recovered to ambient conditions and examined by XRD, TEM, EPMA and SEM. The Rietveld structure refinement was performed in order to derive the structural parameters. We also measured elastic moduli and hardness of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ [14]. In particular, B_0 and B'_0 were determined from the EOS, $V(P)$, measured at RT up to 45 GPa. Nanoindentation technique was applied in order to obtain the reduced elastic modulus, E_r, and hardness, H. From the experimental results for B_0 and E_r we determined the shear modulus, G_0 for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$. Finally, the Vickers microhardness of the obtained porous material has been measured at different loads.

## 2. Carbon nitride imide, $C_2N_2(NH)$

2.1. Experimental
In the LH-DAC experiments the starting dicyandiamide was embedded in the NaCl pressure medium within a hole in the preindented stainless steel gasket, squeezed to required pressure and heated with radiation of a CO_2-laser (λ=10.6 μm). The temperature was determined from the thermal radiation spectrum of the heated sample. After synthesis the products were examined *in situ* by Raman spectroscopy. The recovered samples were washed by dissolving NaCl in distilled water and examined using transmission electron microscope (TEM) equipped with an electron energy-loss spectrometer (EELS) and EDX-detector. The content of H, C, and N was estimated using secondary ion mass spectroscopy (nano-SIMS). All accompanying calculations were carried out within the framework of the density functional theory using the VASP-code.

2.2. Results and discussion
Treatment of dicyandiamide, $C_2N_4H_4$, at P<27 GPa and T<2000 K resulted in black amorphous products. At higher P-T conditions the formation of a new optically transparent phase having

characteristic Raman spectrum was observed. The TEM investigation of recovered products revealed the presence of crystalline material (figure 1a, b). The average crystallite size was found to increase with pressure and heating duration: extended heating (20 min) at temperatures >2000 K and maximal pressure of 41 GPa resulted in formation of crystallites up to 1-1.5 μm in size (figure 1a). The C:N ratio in the crystals was determined from the EELS spectra to be 0.62±0.06. Moreover, the structure in the energy-loss near-edge (ELNES) region indicated tetrahedrally-directed sp^3 hybridized orbitals for both C and N atoms in the synthesized material [12] (figure 1c). No oxygen was detected by EELS, indicating its concentration below 0.1-1 atom. %. Nano-SIMS measurements revealed the presence of hydrogen in the recovered samples with H:C ratio of 0.5±0.15. Thus, the resulting composition of synthesized material can be expressed by formula C_2N_3H.
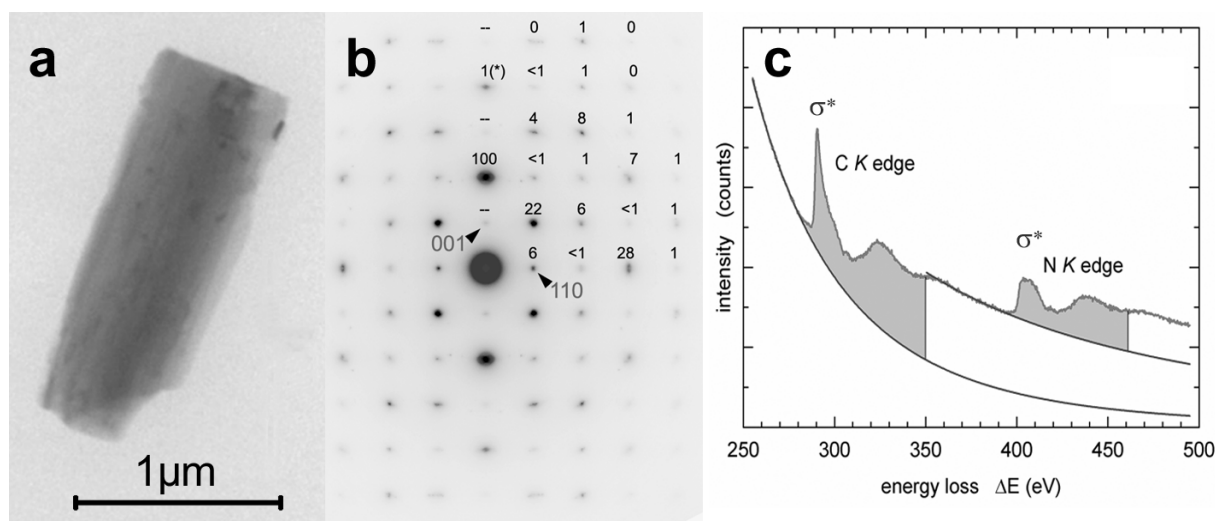
Figure 1. TEM and EELS investigations: (a) Bright field TEM image of the sample synthesized at P=41 GPa and T>2000 K; (b) SAED pattern of zone [$\bar{1}$10] of the C_2N_2(NH). The numbers attached to the reflections are values for kinematic intensities $|F|^2$ scaled to 100 for reflection 002. The intensity of the non-extinct weak reflection 400 (*) is enhanced by secondary diffraction from the 200 reflection; (b) Representative C-K and N-K core-loss edges of C_2N_2(NH) where the grey shaded areas indicate the 60 eV wide integration windows started from the edge onsets. The thick solid lines indicate the power law background fitted in an energy window prior to the edge and extrapolated above it.

The possible crystal structure of the novel C-N-H compound was determined by combination of selected-area electron diffraction (SAED) data, experimentally measured composition and *ab initio* calculations. The structures suggested for hypothetical C_3N_4 [4, 5] were subsequently excluded due to high internal energy, inherent elastic and dynamic instabilities, or by their incompatibility with the observed lattice parameters and the SAED intensities. Only a defect-wurtzite (dwur) structure type gave good agreement with the electron diffraction and EELS data, especially regarding the sp^3-hybridized N sites. Finally, the analysis of SAED patterns for different zone orientations suggested for the new compound, dwur-C_2N_2(NH), the orthorhombic cell with space group $Cmc2_1$, the structure analogous to that of Si_2N_2(NH) or Si_2N_2O. The experimentally determined lattice parameters are in good agreement with calculated values (given in brackets): a=7.546(2) Å [7.5726 Å], b=4.434(8) Å [4.4425 Å], c=4.029(8) Å [4.0036 Å]. The calculated density ρ_{calc} = 3.21 g/cm³ is close but below that of diamond (ρ =3.52 g/cm³). B_0 of C_2N_2(NH) calculated to be 277 GPa is significantly lower than those for diamond or predicted dense C_3N_4 polymorphs (B_0=430-460 GPa).

3. Oxygen-bearing cubic zirconium(IV) nitride, c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$

3.1. Experimental

The HP-HT synthesis of macroscopic amounts of oxygen-bearing c-Zr_3N_4 [13] was performed in a multi-anvil apparatus. As a starting material we used the nanocrystalline powder of nitrogen reach zirconium nitride (Zr:N=1:1.47) having distorted NaCl-type structure [13, 15]. The sample was compressed to 12 GPa and then heated up to 1900 K, kept at the maximum temperature for about 20 minutes and quenched. The sample recovered to ambient conditions was about 1.3 mm in diameter and about 1.5 mm in height. The material was characterized using TEM equipped with an EDX-detector, electron probe micro-analyzer (EPMA) and scanning electron microscope (SEM). The X-ray powder diffractogram (XRPD) was collected from powdered sample using a STOE STADI P diffractometer with Mo-$K_{\alpha 1}$ radiation.

The EOS of oxygen-bearing c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ was measured at RT in a DAC to 45 GPa using quasi-hydrostatic argon pressure medium. The pressure was determined from the EOS of crystalline argon [16]. The specific volumes of the sample and of argon at HP were derived from the EDX diffraction patterns measured using a polychromatic synchrotron radiation on the beamline F3 at the HasyLab (DESY, Hamburg, Germany).

Nanoindentation measurements were performed on a polished surface of the porous polycrystalline c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$. Indentations were done using a Nanoindenter XP equipped with the continuous stiffness measurement (CSM) module [17]. Indentations were performed for two maximum loads of about 23 mN and 14 mN which corresponded to maximal indentation depths of about 260 nm and 210 nm, respectively. Vickers microhardness was measured for loads from 0.49 N to 9.8 N.
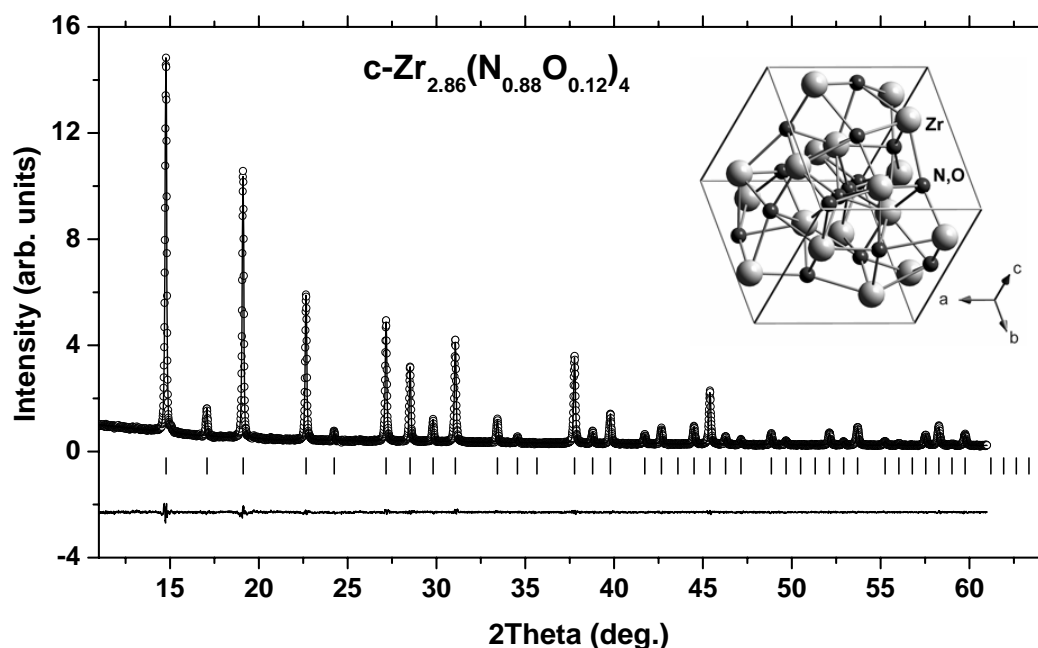

Figure 2. XRPD pattern for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$: observed (open circles) and calculated (solid line) intensities. Their difference curve is given at the bottom of the graph. The calculated peak positions of the Th_3P_4-type structure are denoted by tick marks. Inset: schematic representation of the Th_3P_4-type structure.

3.2. Results and discussion

The XRPD examination of the recovered product showed only lines of a cubic phase which structure could be attributed to that of c-Zr_3N_4 (figure 2). Measurements using EPMA revealed the presence of 2.4(3) wt. % of oxygen. The resulted composition can be expressed by the formula $Zr_{2.86}(N_{0.88}O_{0.12})_4$. Since no amorphous oxidic layer was found on surfaces of the crystallites by TEM, we conclude that oxygen is incorporated in the crystal structure. This observation suggests the formation of an oxygen-bearing cubic zirconium(IV) nitride of the general composition $Zr_{3-u}(N_{1-u}O_u)_4$. The substitution of nitrogen by oxygen at the anion sites of the Th_3P_4-type structure requires, as a consequence of the electrical neutrality condition, the formation of vacancies at the cation sites. This supposition was verified by a full-profile Rietveld structure refinement of the collected XRPD data (figure 2) [13]. The lattice parameter a_0 = 6.7549(1) Å for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ differs slightly from the value 6.740(6) Å reported earlier for c-Zr_3N_4 [7]. We attribute this difference to the presence of oxygen in the crystal structure of the synthesized material.

Farther, we measured the EOS of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ at RT to 45 GPa (figure 3) in a DAC [14]. From the least-square fit of the Birch-Murnaghan EOS [18] to the experimental data we obtained B_0=219(13) GPa and B'_0=4.4(1.0) for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$. For the fixed value of B'_0=4 we obtained B_0=224(5) GPa. The theoretical predictions for B_0 of c-Zr_3N_4 (195-265 GPa) [8-10] scatter around the present value.
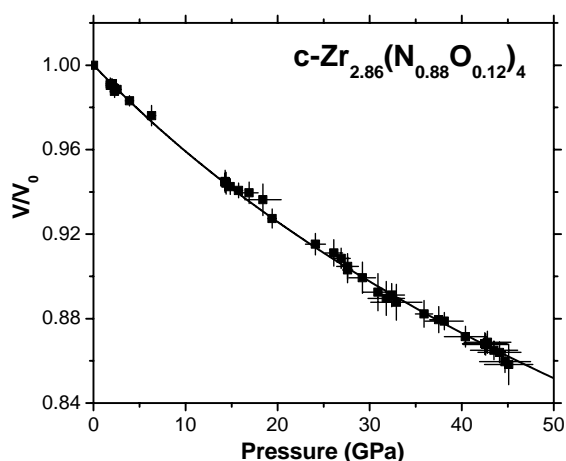
Figure 3. Pressure dependence of V/V_0 of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ measured at RT (■). The solid line represents the least-squares fit of the third-order Birch-Murnaghan EOS to the experimental data.
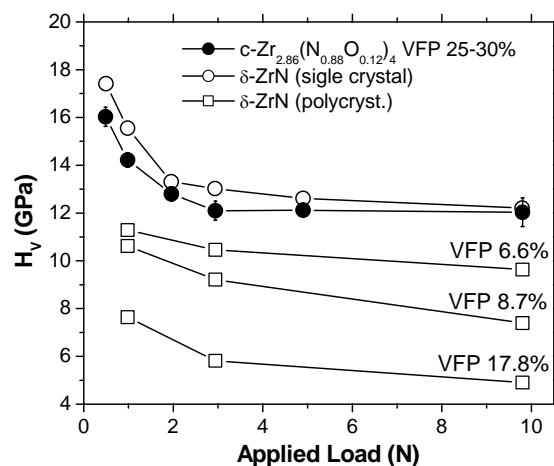
Figure 4. Vickers microhardness of the porous c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ (●) as a function of applied load, compared with hardness of the single crystal (○) [19] and polycrystalline δ-ZrN having different porosity (□) [20].

SEM investigation of the polished sample surface revealed the presence of a chemically homogeneous, porous material with pore sizes of 0.05-2 μm and crystallites of c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ of about 0.8 μm in size. The volume fraction porosity (VFP) was estimated to be about 25-30 %.

From nanoindentation measurements on the polished surface of the porous sample we derived E_r=231GPa and H=18(2) GPa [14]. Using the experimental values for B_0 and E_r and the well known relations between isotropic E_r, E, B, G, and v [21] we determined for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ G_0=96 GPa and E_0=252 GPa [14]. The obtained values should be considered as the lower limits since they could be altered by volume defects in our sample. Despite the apparent porosity, we were able to perform reliable Vickers microhardness measurements for c-$Zr_{2.86}(N_{0.88}O_{0.12})_4$ [13]. The measured H_V(1)=12.0(6) GPa is slightly differs from hardness of single crystal δ-ZrN (12.2 GPa) [19] and

significantly higher than that of even less porous polycrystalline δ-ZrN [20] (figure 4). Based on the known hardness-porosity relations for hard ceramic materials [20, 22, 23], we estimated the Vickers microhardness value of fully dense c-Zr_3N_4 to exceed 30 GPa.

4. Acknowledgments

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