Available online at www.sciencedirect.com
SCIENCE DIRECT®
Physica B 358 (2005) 72–76
PHYSICA B
www.elsevier.com/locate/physb

Influence of nitrogen stoichiometry on properties of low-compressibility advanced nitrides

J.E. Lowther*

DST-NRF Centre of Excellence in Strong Materials and School of Physics, University of the Witwatersrand, Jan Smuts Avenue, Johannesburg 2050, South Africa

Received 21 October 2004; accepted 19 December 2004

Abstract

The properties of two classes of recently synthesized advanced nitrides are investigated with the aim of considering how nitrogen stoichiometry affects the cohesive properties of this material. One is the class of cubic nitrides with an I43d structure of which Zr- and Hf-nitrides and the other a hexagonal $P6_3/mmc$ structure and of which MoN and CoN have also recently been synthesized. All materials are considered to have low compressibility and thus speculated to have a high material hardness. Both categories of materials have an underlying nitrogen sublattice structure. Using ab initio techniques the sublattice structure is considered as being a way through which properties of non-stoichiometric forms of these materials can be examined. Consequences of N stoichiometry on the crystal structure and elastic properties of these materials are suggested.

PACS: 61.72.Ji; 71.15.Nc; 71.20.Be

Keywords: Nitrides; Hardness; Ab initio calculation

1. Introduction

Advanced nitrides are rapidly emerging as an important family of materials with enormous potential for a wide variety of novel applications. Second to diamond cubic boron nitride is now the hardest material known to man and silicon nitride in its various forms is emerging as an important material with promising refractory applications. From the fundamental viewpoint the interest in advanced nitrides was inspired by the theoretical prediction over a decade ago that several forms of carbon nitride in the form C_3N_4 have the potential to be harder than diamond and, as important, be less compressible than diamond [1,2]. To date the synthesis of a suitable form of C_3N_4 with which

*Tel.: +27 11 7176829; fax: +27 11 7176879.
E-mail address: lowthert@physics.wits.ac.za (J.E. Lowther).

0921-4526/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2004.12.028

the theoretical prediction can be tested may not yet have been realized.

Recently, a cubic structural form somewhat similar to that predicted for C_3N_4 has been investigated with a metal such as Zr or Hf in the place of C and where M cations (i.e. Zr or Hf) are eightfold coordinated by N anions. This Zr-nitride, as well as the Hf-nitride, has now been synthesized [3] with a cubic structure and the properties investigated theoretically [4] for the perfectly stoichiometric system. Nitrogen stoichiometry in some other forms of Zr-nitride films seems to influence the final phase of the nitride [5] that is formed and significantly influence related optical properties [6]. Undoubtedly it will be the nitrogen stoichiometry that will influence the physical properties of advanced nitrides of which the compressible character is one of the most important. Given that the Zr and Hf nitrides are considered as being a potentially important new system of nitrides with important physical properties—especially hardness—some indication as to how the material behaves with nitrogen stoichiometry would point to any potential shortcomings that may be encountered should the final material not be exactly stoichiometric.

Another family of nitrides again with a behavior depending on nitrogen stoichiometry are the Mo or Co nitrides. McMillan [7] has made the interesting suggestion that MoN in the hexagonal form may also display a very low compressibility comparable to diamond. More recent hardness studies on MoN films [8] and the bulk material [9] have also suggested that MoN has a very high hardness—especially in the hexagonal structure an observations consistent with McMillan's suggestion of high bulk modulus. Static high-pressure synthesis was suggested as being a mechanism to include large quantities of N into the hexagonal structure [7,10,11] as well as shock compaction [12]. Hence in this technological system of materials the N stoichiometry would be an important feature in dictating the ultimate properties of this system.

At first glance, the Zr and Hf cubic nitrides and the Mo and Co nitrides considered above appear to be rather different as far as the crystal structure is concerned. In fact they have a rather similar feature as in both cases N forms a distinct sublattice. In this paper, we exploit this aspect of the structure and model two situations of N stoichiometry in which the overall nominal symmetry (i.e. hexagonal or cubic) of the crystal lattice is maintained in such a way as to retain the nominal crystal symmetry. In this way some suggestions regarding properties of the non-stoichiometric material can be deduced and also possible ways that the N stoichiometry could be observed are predicted.

2. Crystallographic model

We start by considering the cubic Zr_3N_4 or Hf_3N_4. This material has been assigned to a cubic space group with atoms located at the fractional positions:

$$\begin{aligned} &\text{Zr} \quad (p, 0.0, 0.25),\\ &\text{N} \quad (x, x, x),\\ &\text{N} \quad (y, y, y), \end{aligned}$$

and when $y - x = 0.25$ the symmetry is then I43d.

The other system we investigate is the MoN and CoN system which has a hexagonal symmetry with atoms located at:

$$\begin{aligned} \text{Mo}: \quad & (u, v, w); \quad \left(\tfrac{1}{2} - u, \tfrac{1}{2} - v, \tfrac{1}{2} + w\right),\\ & \left(u, \tfrac{1}{2} + v, \tfrac{1}{2} + w\right); \quad \left(\tfrac{1}{2} - u, 1 - v, 1 - w\right),\\ & \left(\tfrac{1}{2} + u, \tfrac{1}{2} - v, \tfrac{1}{2} + w\right); \quad \left(1 - u, \tfrac{1}{2} - v, \tfrac{1}{2} + w\right),\\ & \left(\tfrac{1}{2} + u, \tfrac{1}{2} + v, \tfrac{1}{2} - w\right); \quad (1 - u, 1 - v, 1 - w),\\ \text{N}: \quad & (0, 0, 0); \quad \left(0, \tfrac{1}{2}, \tfrac{1}{2}\right); \quad \left(\tfrac{1}{2}, 0, 0\right); \quad \left(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\right),\\ & \left(0, 0, \tfrac{1}{2}\right); \quad \left(0, \tfrac{1}{2}, 0\right), \left(\tfrac{1}{2}, 0, \tfrac{1}{2}\right); \quad \left(\tfrac{1}{2}, \tfrac{1}{2}, 0\right), \end{aligned}$$

and the condition for overall P63/mmc symmetry is that $u = \frac{1}{6}$, $v = \frac{1}{3}$, $w = \frac{1}{4}$.

In the first case (Zr_3N_4 or Hf_3N_4) the N atoms are on a BCC lattice, whereas in the second case (MoN and CoN) atoms lie on a simple orthorhombic lattice that in actual fact, as we shall see from the geometry optimization, is also very nearly a simple FCC cubic lattice. Metal atoms essentially are located at appropriate positions within the unit cell and it is the positions of these