Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Solid State Chemistry 181 (2008) 158–165
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Synthesis, stoichiometry and thermal stability of Zn_3N_2 powders prepared by ammonolysis reactions

Giordano Paniconi[a], Zlatka Stoeva[a,1], Ronald I. Smith[b], Patricia C. Dippo[c], Bryan L. Gallagher[d], Duncan H. Gregory[e,*]

[a]*School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[b]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK*
[c]*Measurements and Characterization Division, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401, USA*
[d]*School of Physics and Astronomy, University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[e]*Department of Chemistry, WestCHEM, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK*

Received 16 October 2007; accepted 1 November 2007
Available online 13 November 2007

Abstract

Zn_3N_2 powders were prepared by ammonolysis reactions at 600 °C and examined by thermogravimetric analysis, powder X-ray and neutron diffraction. The powders obtained in this way are unstable in an oxygen atmosphere above 450 °C. In an argon atmosphere, the powders are stable up to their decomposition point at around 700 °C. Structural models obtained from Rietveld refinements against the powder neutron diffraction data indicate that the Zn_3N_2 powders so-prepared have the *anti*-bixbyite structure and are almost certainly stoichiometric with no compelling evidence of nitrogen vacancies. Further, no evidence was found for aliovalent oxygen substitution at the nitrogen sites. The calculated bond valence sums imply that Zn_3N_2 cannot be described as a 100% ionic compound. The structural findings are supported by photoluminescence measurements that reveal a band gap of approximately 0.9 eV.

Keywords: Zinc nitride; Powder neutron diffraction; Stoichiometry; Nitrogen vacancies; Ammonolysis

1. Introduction

Zn_3N_2 is a group II–V semiconducting compound which is currently attracting significant research interest because of its promising electronic and photonic properties. Zn_3N_2 was first examined in 1940 by Juza et al. [1,2] who reported that this compound crystallises in the *anti*-bixbyite structural type. The precise crystal structure was later refined by Partin et al. [3] using time-of-flight (TOF) powder neutron diffraction (PND) data. In the cubic *anti*-bixbyite structure, the metal atoms are in tetrahedral sites of an approximately cubic close packed array of nitrogen atoms. The zinc atoms occupy general crystallographic positions whereas the nitrogen atoms occupy two different sites. The *anti*-bixbyite structure is adopted by several other nitrides, including Mg_3N_2, Be_3N_2 and Cd_3N_2 [1–3].

Zn_3N_2 can be synthesised by several methods, each of which yields products of differing morphologies. Juza et al. [2] reported the preparation of polycrystalline Zn_3N_2 either by the thermal decomposition of $Zn(NH_2)_2$ or via the ammoniation of zinc powder at 600 °C. More recently, Zong et al. [4] prepared Zn_3N_2 powder by a nitridation reaction of Zn powder with NH_3 gas at 600 °C for 120 min. Polycrystalline Zn_3N_2 and $Zn_xN_yO_z$ thin films can be obtained by reactive radio frequency magnetron sputtering [5,6] or by annealing zinc metal films in an NH_3 flow at 410 °C [7]. Furthermore, recently Zn_3N_2 was synthesised in other interesting and unusual morphologies, including nanowires [8] and empty balls [9].

Although Zn_3N_2 was first studied more than 60 years ago, details about its electronic and optical properties have emerged only recently. Futsuhara et al. [6] established that Zn_3N_2 obtained by magnetron sputtering is an *n*-type

---

[*] Corresponding author. Fax: +1 44 141 3304888.
E-mail address: D.Gregory@chem.gla.ac.uk (D.H. Gregory).
[1] Present address: Cambridge Enterprise, University of Cambridge, 10 Trumpington Street, Cambridge CB2 1QA, UK.

0022-4596/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2007.11.005

semiconductor with a direct band gap of 1.23 eV. The same authors also reported that the Zn_3N_2 films obtained in this way showed high electronic mobility of about $100\,cm^2\,V^{-1}\,s^{-1}$ at room temperature. Kuriyama et al. [7] on the other hand, found that Zn_3N_2 has a band gap of 3.2 eV. In the latter case, the Zn_3N_2 films were prepared by direct reaction between NH_3 and Zn layers evaporated on quartz substrates. Kuriyama et al. [7] proposed that the large band gap of Zn_3N_2, as compared to other II–V compounds, originates from the larger ionicity of the Zn–N bond. The value of the band gap for Zn_3N_2 remains debatable. Recently, changes in the band gap energy were attributed to unintentional doping due to oxygen contamination of Zn_3N_2 films grown by metalorganic chemical vapour deposition and radiofrequency molecular beam epitaxy [10].

In view of the applications of Zn_3N_2 and the contradictory reports of its electronic properties, it is of interest to examine the structure–property relations in more detail. Structural details are particularly relevant to the electronic and optical properties of Zn_3N_2: nitrogen vacancies and/or excess metal atoms lead to the generation of free electrons which determine the type of conduction, whereas the concentrations of free electrons (the charge carrier numbers) determine the levels of electronic conductance. Similarly, oxygen substitution at the nitrogen site is expected to influence the electronic properties and the optical band gap.

In this work, we have used PND to examine the stoichiometry of Zn_3N_2 powders prepared by ammoniation in terms of both nitrogen deficiency and oxygen substitution at the nitrogen site. Previously, these structural details have been deduced from X-ray measurements [17]. With the exception of the investigation carried out by Partin et al. [3], no neutron diffraction studies have been reported as yet. Moreover, the effect of the synthesis conditions on the crystal structure and the issue of stoichiometry in Zn_3N_2 were not examined in this previous neutron study [3]. In the present article, we describe our studies to establish the precise structural details for Zn_3N_2 and relate them to both the preparation conditions and the properties of the materials so produced.

2. Experimental

The Zn_3N_2 powders were synthesised by reacting Zn dust of particle size 5–10 μm (Aldrich, 98 + %) with NH_3 gas (BOC, purity 99.999%) at 600 °C. Examination of the Zn dust by X-ray diffraction (XRD) gave no evidence for the presence of crystalline impurity phases. The ammonia gas was additionally dried by passing through a bottle filled with CaO. The reactions were carried out in a Carbolite™ tube furnace fitted with a quartz reaction tube of length 70 cm and internal diameter 2.9 cm. In each reaction, 1.5–2.0 g zinc dust was placed in an alumina boat and transferred to the furnace where ammonia gas was passed over it at a flow rate 500–700 ml min^{-1}. All syntheses included initial preheating at 450 °C for 15 min under flowing ammonia followed by heating at 600 °C for specified reaction times. At the end of each reaction, the furnace was switched off and the products left to cool to ambient temperature in an inert atmosphere, by replacing the ammonia gas with argon (BOC, purity 99.9995%). After each reaction, some amount of zinc was found condensed on the inside surface of the quartz tube. This explains the relatively low yield from the ammonolysis reactions that varied between 60% and 65 wt% of the theoretical amount, according to

$$3Zn + 2NH_3 \rightarrow Zn_3N_2 + 3H_2. \quad (1)$$

The nitrogen content in the Zn_3N_2 samples was determined by elemental analysis using a CE440 elemental analyzer with a thermal conductivity detector from Exeter Analytical Ltd.

Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT-Q600 balance. TGA scans were carried out under oxygen and argon gas flows. The samples, typically 25–35 mg were contained in open alumina crucibles. In all cases, the heating rate was 5 °C/min from 25 to 1000 °C and the gas flow was 60 mL min^{-1}.

Phase purity was assessed from powder X-ray diffraction (PXD) data collected on a Philips XPERT θ–2θ diffractometer with monochromated Cu$K\alpha$ radiation ($\lambda = 1.5405$ Å). The 1-h scans over the range 10–80° 2θ were cross-referenced to powder patterns generated from the inorganic crystal structure database (ICSD) using Powdercell 3 [12]. As described later, the reaction products consisted of Zn_3N_2 as a main phase, in addition to small amounts of ZnO as an impurity phase. ZnO was always observed to be a by-product in this reaction, as noted by other authors [4,11]. We observed formation of ZnO regardless of the purity of the zinc powder staring material and even in cases where the ammonia gas was dried over two bottles filled with quicklime, CaO. (Conversely, reducing the purity of the ammonia from 99.999% to 99.99% led to phase fractions of ZnO larger by an order of magnitude; typically, ca. 60%.) An alternative potential source of oxygen was considered to be the alumina reaction boat and, indeed, the phase fraction of ZnO in the ammoniation products could be reduced—but not to <5 wt%—by vacuum drying the alumina crucible for 20–24 h before use. A similar phase fraction of ZnO was achieved using degassed BN boats. Further, quartz work tubes were observed to yield the highest phase fractions of nitride under the adopted experimental conditions (vs. e.g. alumina, mullite and steel).

Lattice parameters for the initial assessment of the crystal structure were obtained by indexing the powder patterns using DICVOL91 [13]. Rietveld refinements against PXD data were performed using the general structure analysis system (GSAS) [14]. Initial cycles refined the background coefficients and scale factors, followed by refinement of the lattice parameters. As the refinements progressed, peak width parameters, isotropic thermal