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A neutron diffraction study of oxygen and nitrogen ordering in a kinetically stable orthorhombic iron doped titanium oxynitride

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ABSTRACT

The synthesis of a polycrystalline powder sample of iron doped orthorhombic titanium oxynitride, $Ti_{2.92}Fe_{0.01}O_{4.02}N_{0.98}$, on the scale of 0.7 g has been achieved. This was conducted by the unusual route of delamination from a steel substrate of a thin film deposited using atmospheric pressure chemical vapour deposition. The structure of the titanium oxynitride is presented, determined from a combined analysis of X-ray and neutron powder diffraction data. The use of neutron diffraction allows the position of the oxygen and nitrogen ions in the material to be reported unambiguously for the first time. In this study $Ti_{2.92}Fe_{0.01}O_{4.02}N_{0.98}$ is found to crystallise in the *Cmcm* space group, iso-structural pseudobrookite, with lattice parameters $a=3.81080(6)$ Å, $b=9.6253(2)$ Å, and $c=9.8859(2)$ Å, and contains partial oxygen–nitrogen ordering. Of the three anion sites in this structure one is exclusively occupied by oxygen, while the remaining two sites are occupied by oxygen and nitrogen in a disordered manner. Testing indicates that this iron doped titanium oxynitride is a metastable phase that decomposes above 700 °C into TiN and TiO_2, the thermodynamic products.

1. Introduction

Mixed anion solid state materials such as oxynitrides and oxychalcogenides are of interest to researchers because of the greater structural complexity that the additional anion allows, and the concomitant affect this has on the electronic structure and properties [1–4]. The importance of this research area has been highlighted by the recent identification of oxypnictides as high temperature superconductors [5].

The majority of solid state oxynitride phases are synthesised by reaction of an oxide precursor with either ammonia, at temperatures typically greater than 800 °C [3,6,7], or by direct reaction with nitrogen gas at even higher temperatures [8,9]. These approaches have successfully allowed the synthesis of a limited number of ternary transition metal oxynitrides, including those of titanium, vanadium, tungsten and niobium which adopt the $M(O_xN_y)$, $x+y=1$, rock salt structure [10–12]. Others, such as Zr_2ON_2 and Hf_2ON_2 take the bixbyite structure [13]. Tantalum oxynitride, TaON, has been identified in two confirmed polymorphs taking the monoclinic baddeleyite and VO_2(B) structures [14,15]. It has also been possible to synthesis oxynitrides using a non-oxide starting material in a reaction with water saturated ammonia at 900–1000 °C such as the synthesis of Ta_3O_6N from TaS_2 and Zr_7O_8N from $ZrCl_4$ [16,17]. However, the high temperatures used in all these examples mean that only the thermodynamic products are accessible. Any metastable, kinetic products will be difficult to identify by these routes. In contrast, more recent examples of lower temperature syntheses have indentified both a vanadium and titanium oxynitride which do not adopt the long known and thermodynamically stable rock-salt structures. Instead these kinetically stable oxynitrides, $V_3O_{4.61}N_{0.27}$ and $Ti_{2.85}O_4N$, adopt the pseudobrookite-type structure [18,19].

The orthorhombic titanium oxynitride, $Ti_{2.85}O_4N$, was discovered using a novel technique based on chemical vapour deposition, carried out at 600 °C [18] whereby there was an initial deposition as a thin film, which was then delaminated to yield a powder from which the structure was determined by X-ray diffraction. The material has been determined to be a photocatalyst [20], and is also the subject of a high-pressure study [21]. The related oxide, Ti_3O_5, is found at room temperature to adopt a pseudobrookite-like structure which is monoclinic, but above 241 °C adopts the true, orthorhombic pseudobrookite structure [22]. It is this high temperature polymorph that is isostructural to $Ti_{2.85}O_4N$, which can therefore be considered a nitrogen for oxygen substituted form of Ti_3O_5, in which the substitution reduces the monoclinic to orthorhombic structural transition to below room temperature. Cationic substitution of the form

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$M_xTi_{3-x}O_5$ where M=Li, Mg and Fe had been previously shown to also reduce the structural transition temperature so that the pseudobrookite structure was observed at room temperature [23–26]. For both cationic and anionic substitution it is lowering of the Fermi level that induces the structural change.

In the previously reported synthesis of $Ti_{2.85}O_4N$ the sample was made by delamination of a thin film from a glass substrate, producing a 25 mg sample for which the structure and composition were confirmed by XRD and XPS. However, there was still some uncertainty as to the presence of any oxygen or nitrogen ordering due to the similarity in X-ray scattering factor for the oxide and nitride ions. This was unfortunate because the similar size and polarizability of the oxide and nitride ions mean that they can occupy the same crystallographic sites, but structural complexity may still result depending on whether the two different ions are ordered or disordered across those sites. For example, most compounds with isotopic structures and similar anion sites (coordination number, bond lengths) show disordered occupation by oxygen and nitrogen, and these include perovskite structures, such as $LaAO_2N$, (A=Ti, Zr) $BaBO_2N$, (B=Ti, Zr) and $NdTiO_2N$, [8,27,28], or the bixbyite structured $ZrON_2$, in which all the anion are 4 coordinate [13]. Ordering of oxygen and nitrogen is more common in structures with different anion sites, such as in both β and γ TaON, containing mixtures of 3 and 4 and 2, 3 and 4 coordinate anion site, respectively. In each case nitrogen is preferentially found on the higher coordination number sites [14,15]. However ordering can also be found in isotopic structures like the perovskites $SrTaO_2N$ and $CaTaO_2N$ [29], if the synthesis temperature is sufficiently low to prevent randomisation. Neutron diffraction data provides the most reliable method to resolve the position of the oxide and nitride ions due to the significant difference in coherent neutron scattering power for the two elemental nuclei, unfortunately the previously prepared sample of $Ti_{2.85}O_4N$ was of insufficient mass to conduct a neutron experiment.

In this paper a modified synthesis of the titanium oxynitride is presented making use of a steel rather than glass substrate. This has allowed the production of a much larger sample size upon which neutron diffraction experiments have been conducted, the analysis of which has allowed the presence of partial oxygen–nitrogen ordering to be observed. Portions of this sample have also been tested for thermodynamic stability in air and vacuum up to 1000 °C, the results of which will indicate that the traditional high temperature synthetic methods of nitridation would not be suitable in the synthesis of this titanium oxynitride.

2. Experimental methods

A thin film of the titanium oxynitride was synthesised using a cold walled atmospheric pressure chemical vapour deposition reactor, of which details have previously been published [18]. Titanium (IV) chloride (Aldrich 99.9%), ethyl acetate (BDH, GPR grade) and ammonia (BOC, anhydrous) were used as precursors and sources of titanium, oxygen and nitrogen. Titanium (IV) chloride and ethyl acetate were supplied from bubblers heated to 82 °C and 37 °C and transported using N_2 (BOC, oxygen free) carrier gas flows of 1.0 $dm^3\ min^{-1}$ and 0.5 $dm^3\ min^{-1}$, respectively. The ammonia was supplied under its own vapour pressure at a rate of 0.2 $dm^3\ min^{-1}$. An additional plain flow of N_2 at a rate 12 $dm^3\ min^{-1}$ was added as a diluent to the precursor laden gas flows at the point where they were combined before entry into the reactor. The deposition took 15 min and was carried out onto a stainless steel substrate of dimensions $90 \times 227 \times 0.5\ mm^3$, held at a temperature of 650 °C.

The use of a steel substrate allowed complete delamination of the film as the coated steel was flexed causing the brittle ceramic coating to peel off the surface. The fragments of film were then collected and ground in an agate pestle and mortar. This yielded 0.7 g of a dark-green powder.

Neutron diffraction was carried out with this powder sample using the *GEM Xpress* service on the GEM time-of-flight instrument at the ISIS pulsed neutron facility [30]. The data were collected using 6 banks of detectors covering scattering angles of 9–154°. The data were used in a Rietveld refinement carried out with the EXPGUI interface for the GSAS suite of software packages [31,32]. Additionally powder X-ray diffraction data were collected using a Bruker D8 instrument, utilising Cu K_α radiation. Scanning electron microscope imaging and energy dispersive X-ray analysis measurements were conducted using a JEOL 6301 field emission SEM.

After the neutron experiment had been concluded 0.025 g portions of the sample were tested for thermodynamic stability in air and under vacuum. For the air stability test the samples were placed in alumina crucibles and heated in a furnace for 48 h. For the vacuum stability test the samples were sealed using a dynamic vacuum in silica ampoules under a pressure of less than 10^{-2} mbar, then the ampoules placed in a furnace for 48 h. Both air and vacuum experiments were carried out at eight temperatures from 300 °C to 1000 °C at 100 °C intervals. After firing all samples were analysed using X-ray powder diffraction.

3. Results and discussion

A powder sample of titanium oxynitride was derived from a single delaminated film deposited onto a steel substrate by CVD from titanium(IV) chloride, ethyl acetate and ammonia. This produced a powder sample of 0.7 g, considered sufficient for a neutron diffraction experiment, carried out on the GEM instrument at the ISIS neutron source. It was also analysed using SEM and EDX.

3.1. SEM analysis

During the synthesis the adventitious difference in malleability of the synthesised compound and the steel substrate was used to completely delaminate the film and procure a sufficient quantity of powder product for a neutron diffraction experiment. However this method did lead to concern about contamination of the product with iron from the stainless steel substrate. In order to determine if iron was present in the film, energy dispersive X-ray analysis measurements were carried out using an SEM instrument. Iron contamination was a particular concern with this compound because monoclinic Ti_3O_5 can also be stabilised in its orthorhombic pseudobrookite form by cationic substitution of iron, as opposed to the anionic substitution targeted in this work – with Fe_2TiO_5 being pseudobrookite itself.

Energy dispersive X-ray spectra were collected from 16 spots on different powder particles, and additionally four wide area scans, each across a number of powder particles, were taken. The area analysis gave an average iron content of 1.6(4) % of the total metal content, while the average from the spot analysis was 1.8(6)%. This indicates that some contamination from the substrate did occur, in contrast to the initial work in which glass substrates were used, for which XPS measurements recorded that no other metals were present within the detection limit of the technique ($< 0.5\%$). This small presence of iron, however, is not likely to be a controlling factor in determining the structure. The *Cmcm* structure for $Ti_{3-x}Fe_xO_5$ is only stable at room temperature with an iron content of above $x > 0.3$, or 10% metal basis, as such