Communications

New Zirconium Titanium Oxynitrides Obtained by Ammonolysis of Zirconium Titanate

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The lower electronegativity of nitrogen compared with oxygen often leads to lower transition metal oxidation states and more covalent bonding in nitrides and oxynitrides than in oxides. It is attractive to tune the properties of a material by changing the O/N ratio, and the degree of crystallographic order between oxide and nitride anions and/or between anions and vacancies. The synthetic challenges associated with this chemistry mean that there are few well-characterized ternary transition metal oxynitrides; most of these are insulators containing an alkaline earth or lanthanide and a fully oxidized early transition metal.[3] Here we describe the structure, properties, and unusual reoxidation characteristics of new partially reduced ternary oxynitrides containing two early transition metals which evolve in structure from vacancy-disordered fluorite type to vacancy-ordered bixbyite type as the O/N ratio decreases.
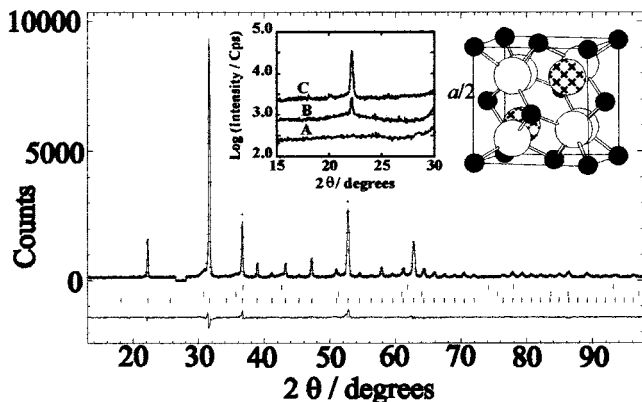
Black oxynitrides in the continuous composition range between $ZrTiO_{1.92(3)}N_{1.23(3)}$ and $ZrTiO_{1.06(3)}N_{1.90(3)}$ with metallic luster and mean metal oxidation states of 3.8-(1) were obtained by ammonolysis of α-PbO$_2$-type ZrTiO$_4$[4] at temperatures between 700 and 900 °C. Higher synthesis temperatures and longer reaction times decreased the O/N and anion/cation ratios. The X-ray powder diffraction (PXRD)[5] pattern of $ZrTiO_{1.92(3)}N_{1.23(3)}$ (735 °C, 3 × 20 h) is characteristic of a material with the fluorite structure ($a = 4.9505(4)$ Å) and a large concentration of disordered anion vacancies. It should be noted that the substitution of oxide ions by nitride ions and vacancies is not topotactic: α-PbO$_2$-type ZrTiO$_4$ has a hexagonal "close packed" array of anions with cations in half the octahedral sites, while the fluorite-related products have a simple cubic array of anions with cations in eight-coordinate sites. Binary fluorite-related zirconium oxynitrides with similar anion/cation ratios only have disordered anions and vacancies at high temperatures,[6] so substitution of Ti for Zr stabilizes the vacancy-disordered fluorite structure at these compositions. Materials synthesized at temperatures between 750 and 850 °C (e.g., $ZrTiO_{1.30(2)}N_{1.73(2)}$ 750 °C, 2 × 20 h; 850 °C, 18 h) show diffuse scattering accompanying

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(3) Marchand, R.; Laurent, Y.; Guyader, J.; L'Haridon, P.; Verdier P. *J. Eur. Ceram. Soc.* **1991**, *8*, 197.

(4) ZrTiO$_4$ was prepared by reacting 5 g (41 mmol) of ZrO$_2$ (Aldrich 99.9%) with an equimolar amount of TiO$_2$ (Aldrich 99.99%) for 24 h at 1500 °C in air. Powder X-ray diffraction indicated phase-pure ZrTiO$_4$ with complete cation disorder[8] in the α-PbO$_2$-type structure with both cations six-coordinate. Oxynitrides were prepared by reacting finely ground ZrTiO$_4$, in an alumina boat, with ammonia gas (British Oxygen Company 99.98%) flowing along a 25 mm diameter silica tube at approximately 14 dm^3 h^{-1} in a split tube furnace. Reactions were carried out at temperatures between 700 and 900 °C for periods of about 20 h, with regrinding between heating periods, as specified in the text. After reaction, the tube was isolated from the ammonia flow and removed from the furnace so that the sample cooled to room temperature without being exposed to air. The oxynitrides were inert to O$_2$ or moisture at room temperature and to prolonged boiling in water. Composition was determined using combustion analysis for nitrogen and thermogravimetric analysis (mass gain on heating 25 mg of sample to 1100 °C in air using a STA 1500H TGA/DSC instrument).

Figure 1. Rietveld analysis using GSAS[5] of powder X-ray diffraction data for $ZrTiO_{1.06(3)}N_{1.90(3)}$. (Observed (+), calculated (−) and difference (bottom)). The impurity phases were included in the refinement: the three sets of vertical tick marks are for $ZrTiO_{1.06(3)}N_{1.90(3)}$ (90.2(5)%, lower) and a fluorite structure zirconium oxynitride (4.4(1) %, middle) and TiN (5.5(5)%, upper). A weak reflection arising from the silicon wafer used as the sample holder has been excluded from the refinement. Insets: one-eighth of the bixbyite unit cell (cell constant, *a*) showing the relation to the fluorite unit cell (cations, small circles; anions, large open circles; anion vacancies, large hatched circles); low-angle powder X-ray diffraction data (note the logarithmic scale) for $ZrTiO_{1.92(3)}N_{1.23(3)}$ (A), $ZrTiO_{1.30(2)}N_{1.73(2)}$ (B), and $ZrTiO_{1.06(3)}N_{1.90(3)}$ (C). Diffuse scattering in the N-poor fluorite phases prepared at low-temperature develops into superstructure reflections (bixbyite 211 reflection is shown) characteristic of the vacancy ordered bixbyite structure in N-richer phases synthesized at higher temperatures.

weak superstructure reflections in their PXRD patterns (Figure 1 inset), indicative of short-range ordering of the anion vacancies. Intense superstructure reflections and a lack of diffuse scattering in materials synthesized above 850 °C indicate full anion/vacancy ordering similar to that in binary zirconium oxynitrides.[6] The PXRD pattern of $ZrTiO_{1.06(3)}N_{1.90(3)}$, (760 °C, 2 × 20 h; 820 °C, 20 h; 860 °C, 20 h), was indexed according to the bixbyite (C-M_2O_3) structure,[7] which is derived from fluorite by removal of one-quarter of the anions in an ordered fashion (Figure 1 inset) leading to a $2a \times 2a \times 2a$ body centered cubic superlattice. During ammonolysis above 900 °C or postsynthetic annealing at 800 °C, phase separation to TiN and a fluorite-related zirconium oxynitride occurred. Partial phase separation occurred above 800 °C, indicating that the ternary oxynitrides are only metastable at these temperatures.

Rietveld analysis, using GSAS,[5] of laboratory PXRD data[5] for $ZrTiO_{1.06(3)}N_{1.90(3)}$ (Figure 1) confirmed the bixbyite structure (space group $Ia\bar{3}$ (no. 206), $a = 9.8231(3)$ Å) and indicated no Zr/Ti order between the two metal sites (site 1, six cation−anion distances of
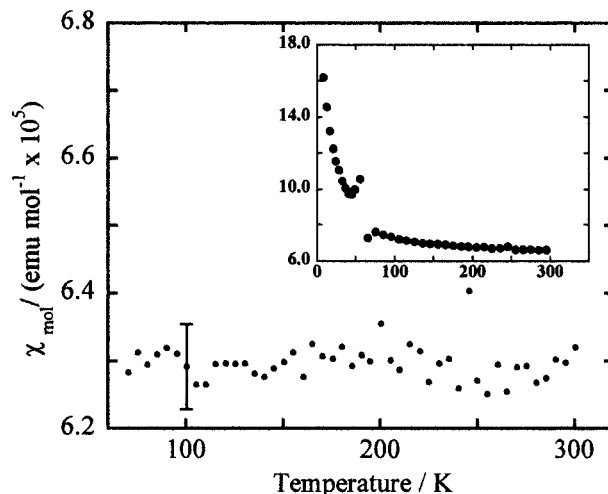
Figure 2. The magnetic susceptibility of $ZrTiO_{1.81(2)}N_{1.32(2)}$ (which contained no TiN by PXRD) fit to $\chi = \chi_0 + C/T$ above 70 K. Corrections were made for sample container and core diamagnetism contributions. The small Curie term has been subtracted here. The origin of the anomaly at about 50 K (inset shows data plotted over the entire temperature range measured) is currently under investigation; it is not due to condensed O_2. Below the anomaly the data may be fit to $\chi = \chi_0 + C/(T - \theta)$ with χ_0 unchanged within error from its high-temperature value, C corresponding to 0.3% $S = 1/2$ impurity spins and $\theta = -15(1)$ K.

2.098(4) Å; site 2, three pairs of cation−anion distances of 2.084(5), 2.117(7), and 2.156(5) Å), consistent with the reluctance of the two metals to order in $ZrTiO_4$.[8] There is no O/N ordering in the isostructural Zr_2ON_2.[9] The closest metal−metal distances are 3.2399(8) and 3.2580(6) Å.

Partial phase separation during synthesis at the higher temperatures, leading to contamination by TiN, prevented us from making reliable physical property measurements on the more nitride-rich phases. The magnetic susceptibility[10] (Figure 2) of $ZrTiO_{1.81(2)}N_{1.32(2)}$, (760 °C, 15 h, phase-pure by PXRD) with the vacancy-disordered fluorite structure, may be fit, above 70 K, to $\chi = \chi_0 + C/T$ with a Curie term corresponding to 0.3% $S = 1/2$ spins which may arise from a small amount of a paramagnetic impurity. The dominant temperature-independent term, χ_0, is $6.30(1) \times 10^{-5}$ emu mol^{-1} after correction for the container and for core diamagnetism. The susceptibility is of the same order as that of metallic titanates such as $LiTi_2O_4$,[11] suggesting that the 3d electrons introduced on reduction are delocalized. Assuming this delocalized character, the density of states at the Fermi level, $n(E_F)$, is 1.0 orbital states per electronvolt per Ti, larger than the 0.48 orbital states per electronvolt per Ti calculated using the nearly free electron model, taking into account t_{2g} orbital degeneracy correctly, indicating that the conduction band is narrower than this simple model predicts. It was not

(5) Powder X-ray diffraction measurements were made using a Siemens D5000 diffractometer operating in Bragg−Brentano geometry with Cu Kα_1 radiation (Ge (111) monochromator). The sample was mounted on a silicon wafer with a small amount of silicone vacuum grease. Data for Rietveld refinement using GSAS (Larson, A.; von Dreele, R. B. *The General Structure Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 1985) were collected in the range 5−100° 2θ with a step size of 0.03° and for 80 s per point. For $ZrTiO_{1.06(3)}N_{1.90(3)}$ (Figure 1) the goodness of fit, χ^2, was 0.93 and the weighted profile R factor, R_{wp}, was 0.078.

(6) Lerch, M. *J. Mater. Sci. Lett.* **1998**, *17*, 441.

(7) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984.

(8) McHale, A. E.; Roth, R. S. *J. Am. Ceram. Soc.* **1986**, *69*, 827.

(9) Clarke, S. J.; Michie, C. W.; Rosseinsky, M. J. *J. Solid State Chem.* **1999**, *146*, 399.

(10) Magnetic susceptibilitymeasurements were performed on 90 mg of powder, loaded under He in a gelatin capsule, using a Quantum Design MPMS-5 SQUID magnetometer: subtraction of the magnetic moment measured at 3 T from that measured at 4 T allows elimination of contributions to the susceptibility from tiny amounts of ferromagnetic impurities, as these saturate in fields greater than 1 T.

(11) Harrison, M. R.; Edwards, P. P.; Goodenough, J. B. *Philos. Mag. B* **1985**, *52*, 679.
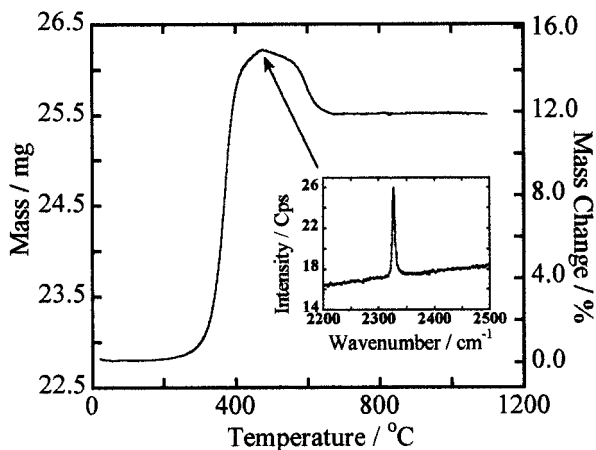
Figure 3. Thermogravimetric analysis in air shows the behavior of $ZrTiO_{1.06(3)}N_{1.90(3)}$ on oxidation. The larger than expected mass between 400 and 700 °C corresponds to the retention of N_2 molecules in the structure. Inset: Raman spectrum in the N_2 stretching region for $ZrTiO_4(N_2)_{0.20}$ obtained by quenching from 420 °C.

possible to sinter a pellet of the material under ammonia at 800 °C because of decomposition, however the resistivities of metallic titanates[12] or metallic oxynitrides,[13] measured as unsintered pressed pellets, are between 0.1 and 10 Ω cm. The resistivity of an unsintered pressed pellet of $ZrTiO_{1.81(2)}N_{1.32(2)}$ was $6(1) \times 10^6$ Ω cm at room temperature. This high value suggests that the 3d electrons are not fully delocalized in the conduction band, while the absence of significant temperature dependence of the magnetic susceptibility rules out Ti^{III} d^1 centers localized by the Mott–Hubbard mechanism. These new phases are appreciably disordered: fluorite structure $ZrTiO_{1.81(2)}N_{1.32(2)}$ may be formulated $MX_{1.57}V_{0.43}$ with both the anions and vacancies disordered. Furthermore, diffraction studies show Zr/Ti and probable O/N disorder.[9] If the range of potentials at each metal site is large compared with the bandwidth then insulating behavior arises from Anderson localization[14] with localized states at the band edges separated from fully delocalized states in the central portion of the band by a mobility edge, E_c. If E_f lies below E_c then the material is an insulator. $ZrTiO_{1.81(2)}N_{1.32(2)}$ contains only 0.2 d

electrons per metal cation, so the conduction band is only 3–4% filled. The data indicate that $ZrTiO_{1.81(2)}N_{1.32(2)}$ is in this Anderson localized regime and the magnetism arises from electrons with energies below E_c.

While TiO_2 is readily reduced by ammonia to TiN, electropositive metals such as La stabilize Ti^{IV} at 1000 °C under ammonia in the synthesis of $LaTiO_2N$ from $La_2Ti_2O_7$.[3,15] The results presented here suggest that zirconium is not sufficiently electropositive to stabilize Ti^{IV}, but does suppress complete reduction to Ti^{III}. The slow reduction of ZrO_2 to ZrN by ammonia requires temperatures above 1000 °C, suggesting that here only Ti is reduced.

Thermogravimetric analysis measurements[4] (Figure 3) show that oxidation to $ZrTiO_4$ in air begins at about 300 °C and is complete by 700 °C. Between 400 and 700 °C, the mass gain measured during oxidation was larger than expected because molecular N_2 units, derived from oxidation of the nitride ions, are kinetically trapped within the structure. Raman spectroscopy[16] (Figure 3, inset) confirmed the presence of N_2 units in the white, fully oxidized material, quenched from 420 °C in air. The absorption frequency $(2330(1)$ $cm^{-1})$ is similar to that in gaseous or liquid N_2, consistent with the inability of the d^0 metals to π-back-bond to N_2. We obtained compositions $ZrTiO_4(N_2)_x$ $(0.1 \leq x \leq 0.2$; larger x for the more N-rich oxynitrides), corresponding to gas pressures of 50–100 atm. This is comparable to the amount of N_2 retained in the oxidation of $LaTiO_2N$ to $LaTiO_{3.5}(N_2)_{0.3}$.[17] The nature of the interaction between N_2 and the metal centers is the subject of ongoing investigation.

(12) Clarke S. J.; Fowkes, A. J.; Harrison, A.; Ibberson, R. M.; Rosseinsky, M. J. *Chem. Mater.* **1998**, *10*, 372.
(13) Fawcett, I. D.; Ramanujachary, K. V.; Greenblatt M. *Mater. Res. Bull.* **1997**, *32*, 1565.
(14) Anderson, P. W. *Phys. Rev.* **1958**, *109*, 1492. Elliott, S. R. *Physics of Amorphous Materials*; Longman: London, 1990.

(15) Marchand, R.; Pors, F.; Laurent, Y. *Ann. Chim. Fr.* **1991**, *16*, 553.
(16) Raman spectroscopy was performed using a Dilor Labram spectrometer with a wavelength of 632.82 nm.
(17) LeGendre, L.; Marchand, R.; Piriou, B. *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 972.