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Direct Solid-State Synthesis at High Pressures of New Mixed-Metal Oxynitrides: $RZrO_2N$ (R = Pr, Nd, and Sm)

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New oxynitrides of $RZrO_2N$ (R = Pr, Nd, and Sm) have been synthesized via a direct solid-state reaction of R_2O_3 with Zr_2ON_2 at 1200−1500 °C under 2−3 GPa pressure. Powder X-ray diffraction shows that all three phases adopt an orthorhombic *Pnma* perovskite superstructure [$a = 5.8537(1)$ Å, $b = 8.1707(1)$ Å, and $c = 5.7093(1)$ Å for $NdZrO_2N$] and the structural distortion increases with decreasing R^{3+} ionic radius. This method may enable new mixed-metal oxynitrides to be synthesized without the use of nitriding gas atmospheres.

Nitride-based materials are less explored than solid oxides because of the lower stability of nitrides, although the O^{2-} and N^{3-} anions show similar chemical, structural, and electronic characteristics. Research on nitrides and oxynitrides has progressed substantially in recent years, in part, because of the development of new synthetic approaches. High-pressure methods have led to the discovery of hard binary nitrides as the spinel Si_3N_4,[1] the Th_3P_4-type Hf_3N_4 and Zr_3N_4,[2] and the first noble metal nitride PtN_2.[3]

Ammonolysis of a precursor oxide or solid-state reactions between oxides under flowing NH_3 gas[4,5] has enabled many new oxynitrides to be synthesized.[6−13] These generally have greater air stability than pure nitrides. Several quaternary transition-metal oxynitride perovskites show notable physical and chemical properties. The solid solutions $Ca_{1-x}La_xTaO_{2-x}N_{1+x}$ are nontoxic inorganic pigments,[6] $BaTaO_2N$ has a high bulk dielectrical constant[9] and photocatalyzes the decomposition of water,[14] and colossal magnetoresistances were recently discovered in $EuNbO_2N$ and $EuWON_2$ at low temperatures.[12,15] However, the synthesis of some mixed-metal oxynitrides is difficult at ambient pressures. Binary rare-earth oxides R_2O_3 do not usually react with transition-metal oxides in NH_3 at moderate temperatures so that the ammonolytic synthesis of rare-earth transition-metal oxynitrides requires the use of ternary oxides, if available, or very reactive, amorphous precursors.[12,16]

Direct high-pressure solid-state reactions without the use of gaseous ammonia or nitrogen atmospheres should be convenient for oxynitride synthesis because pressure suppresses decomposition to oxides and nitrogen. High pressure also stabilizes structures with high coordination numbers such as perovskite. However, very few direct solid-state syntheses of oxynitrides at high pressures have been reported. A novel ternary spinel Ga_3O_3N was synthesized by the direct reaction of Ga_2O_3 and GaN at 5 GPa (50 kbar) pressure and 1500−1700 °C.[17] La_2VO_3N is the only new mixed-metal oxynitride to have been reported, although the structure was not characterized.[18]

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Table 1. Synthesis Conditions and Powder X-ray Diffraction Results (Lattice Parameters and Fitting Residuals) for $RZrO_2N$ (R = Pr, Nd, and Sm)

	$PrZrO_2N$	$NdZrO_2N$	$SmZrO_2N$
pressure/GPa	2	2	3
T/°C	1150	1200	1500
reaction time/h	1	1	0.5
a/Å	5.8440(2)	5.8537(1)	5.8423(2)
b/Å	8.1808(2)	8.1707(1)	8.1281(3)
c/Å	5.7335(1)	5.7093(1)	5.6621(1)
V/Å^3	274.12(1)	273.07(1)	268.88(1)
R_p	0.0181	0.0197	0.0190
R_{wp}	0.0238	0.0253	0.0246
χ^2	1.43	1.34	1.53

Rare-earth zirconium oxynitride perovskites $RZrO_2N$ are of interest as potential dielectrics or multiferroic materials when magnetic R^{3+} and d^0 Zr^{4+} are present. A previous study showed that $LaZrO_2N$ could be synthesized by repeated ammonolysis of a reactive, amorphous $La_2Zr_2O_7$ precursor at 1000 °C, but other R analogues were not accessible.[16] Here we report an alternative, direct high-pressure route that has enabled three new $RZrO_2N$ perovskites (R = Pr, Nd, and Sm) to be synthesized. We have investigated the reaction

$$R_2O_3 + Zr_2ON_2 \rightarrow 2RZrO_2N$$

which makes use of Zr_2ON_2 as a convenient nitrogen source because this phase is more easily synthesized than quaternary zirconium oxynitrides.

Zr_2ON_2 was prepared by the treatment of ZrO_2 (99.99%, Aldrich Chemical Co.) under NH_3 (99.9%, Carburos Metálicos) at a flow rate of 670 cm^3/min.[19] Samples were treated at 1000 °C for 24 h and then quenched at room temperature in ammonia. Their purity was checked by X-ray diffraction, and the nitrogen contents were determined by elemental analysis (Carlo Erba instrument) and thermogravimetric analysis (Perkin-Elmer) in an oxygen atmosphere. The samples used for the high-pressure experiments had nitrogen contents between 1.97 and 2.01 mol per formula unit. Pr_2O_3 was prepared by reducing Pr_6O_{11} (Aldrich Chemical Co., 99.999%) under 5% H_2/N_2 at 1100 °C for 24 h. Nd_2O_3 and Sm_2O_3 (both Aldrich Chemical Co., 99.99%) were dried overnight at 800 °C.

High-pressure reactions were carried out using a Walker-type two-stage multianvil press that can achieve conditions up to 15 GPa and 1500 °C. 1:1 mixtures of R_2O_3 and Zr_2ON_2 with a total mass of approximately 25 mg were finely ground, transferred to a boron nitride capsule, and loaded into the press.[20,21] The sample was compressed over 2 h and then heated to the reaction temperature in 10 min. Following the reaction, the samples were quenched to room temperature, decompressed over 8 h, and carefully separated from the boron nitride capsule.

All of the recovered products were air-stable and were examined by powder X-ray diffraction using Cu Kα_1 radiation. Data for structural analysis were taken in the range $2\theta = 15-115°$ with a 0.007° step size counting for 3 s per step and were Rietveld-fitted using the *GSAS* package.[22]

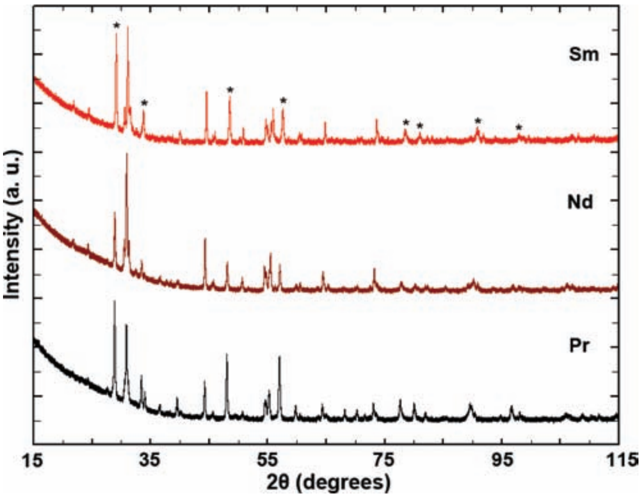

Figure 1. Powder X-ray diffraction patterns of $RZrO_2N$ samples (R = Pr, Nd, and Sm) with prominent peaks from the pyrochlore phase marked with asterisks.

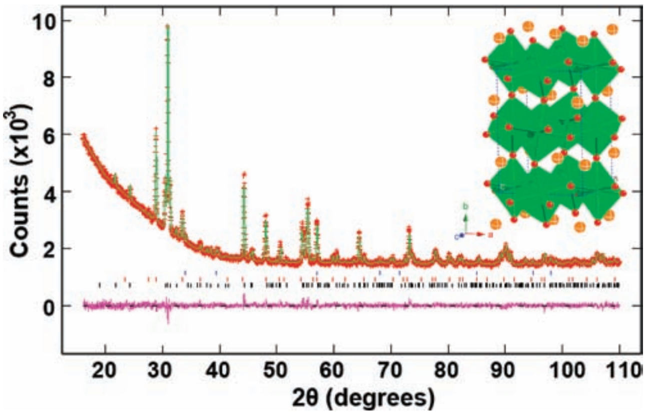

Figure 2. Rietveld fit of the powder X-ray diffraction profile of $NdZrO_2N$. The Bragg reflection markers correspond to ZrN, $Nd_2Zr_2O_7$, and $NdZrO_2N$ from top to bottom. The inset shows the distorted perovskite structure of $NdZrO_2N$.

The reaction between Nd_2O_3 and Zr_2ON_2 was explored at 1−10 GPa and 900−1300 °C. At pressures above 6 GPa, mixtures of ZrN and various metal oxides were formed. Below 6 GPa, mixtures of a new perovskite, $NdZrO_2N$, and a pyrochlore-type phase were observed. The latter could not be completely eliminated by varying the reaction conditions. The cubic lattice parameter of the pyrochlore phase was found to vary in the range 10.62−10.70 Å, around the value of 10.680 Å for $Nd_2Zr_2O_7$. This indicates that the pyrochlore has a variable composition and so may also be a quaternary oxynitride, $Nd_2Zr_2O_{7-x}N_{2x/3}$, because rare-earth transition-metal oxide pyrochlores are known to accommodate substantial nitride contents, e.g., $Sm_2Mo_2O_{3.83}N_{3.17}$.[23] The best sample out of 15 high-pressure runs contained 69% $NdZrO_2N$, 28% $Nd_2Zr_2O_{7-x}N_{2x/3}$, and 3% ZrN and was obtained under the conditions shown in Table 1. Similar conditions were used to obtain a $PrZrO_2N$ sample, but significantly higher pressures and temperatures were required to obtain $SmZrO_2N$.

Figure 1 shows the powder X-ray diffraction patterns of the $RZrO_2N$ samples (R = Pr, Nd, and Sm). Rietveld

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Table 2. Refined Atomic Parameters for $RZrO_2N$ (R = Pr, Nd, and Sm) in Space Group *Pnma*[a]

variables	Pr	Nd	Sm
R: x	0.0442(4)	0.0469(2)	0.0549(5)
R: z	0.9799(7)	0.9857(4)	0.998(2)
R: U_{iso}/Å^2	0.027(1)	0.020(1)	0.023(8)
Zr: U_{iso}/Å^2	0.009(1)	0.015(1)	0.025(1)
O/N1: x	0.466(4)	0.465(2)	0.469(6)
O/N1: z	0.103(3)	0.112(2)	0.126(4)
O/N2: x	0.301(3)	0.314(2)	0.331(4)
O/N2: y	0.061(2)	0.049(1)	0.044(3)
O/N2: z	0.689(2)	0.690(2)	0.650(4)
O/N: U_{iso}/Å^2	0.005(3)	0.012(3)	0.011(3)

[a] The atomic positions are R (x, 0.25, z), Zr (0.5, 0, 0), O/N1 (x, 0.25, z), and O/N2 (x, y, z).

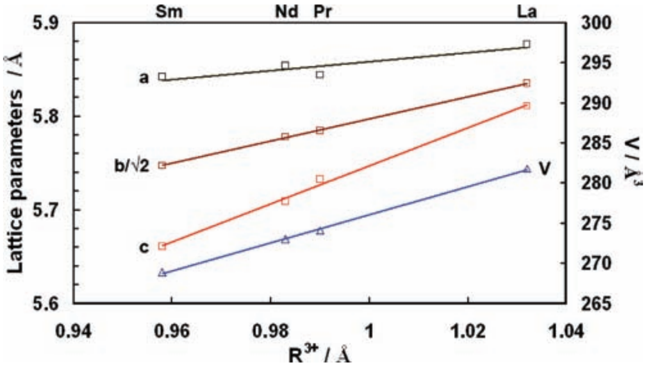

Figure 3. Plots of cell parameters and volume against the R^{3+} ionic radius for R = Sm, Nd, and Pr (this work) and R = La (ref 16).

Table 3. Interatomic Distances (Å) and Angles (deg) for $RZrO_2N$ (R = Pr, Nd, and Sm)

	Pr	Nd	Sm
Zr−O/N1 (×2)	2.13(1)	2.15(1)	2.16(1)
Zr−O/N2 (×2)	2.13(1)	2.11(1)	2.14(2)
Zr−O/N2 (×2)	2.18(1)	2.17(1)	2.24(2)
⟨Zr−O/N⟩	2.15(1)	2.14(1)	2.18(2)
R−O/N1 (×1)	2.43(2)	2.34(1)	2.18(3)
R−O/N1 (×1)	2.56(2)	2.55(1)	2.53(4)
R−O/N2 (×2)	2.31(1)	2.35(1)	2.27(2)
R−O/N2 (×2)	2.71(1)	2.82(1)	2.63(2)
R−O/N2 (×2)	2.96(2)	2.83(1)	3.04(2)
⟨R−O/N⟩	2.62(1)	2.61(1)	2.55(2)
Zr−O/N1−Zr	146.0(1)	143.4(7)	140.1(1)
Zr1−O/N2−Zr	143.2(8)	144.9(5)	136.0(1)

refinements of the perovskite structure and the secondary pyrochlore and ZrN phases give a good fit to the data, as shown in Figure 2. All three $RZrO_2N$ perovskites crystallize in the orthorhombic *Pnma* superstructure, and their refined lattice parameters and atomic positions are shown in Tables 1 and 2. No evidence for O/N order over the two available anion sites was found, although neutron diffraction will be needed to provide reliable anion occupancies.

The plot of cell parameters against the R^{3+} radius in Figure 3 demonstrates that the orthorhombic structural distortion increases as the R^{3+} radius becomes smaller. The 8-fold coordination environment of R^{3+} becomes more distorted as the average ⟨R−O/N⟩ distance decreases from R = Pr to Sm. This results in increasing deformations and tilting of the $Zr(O/N)_6$ octahedra, as shown by the bond distances and angles in Table 3 and the inset to Figure 2. The Zr−O/N−Zr angles are reduced from 180° in the ideal perovskite structure to 136° in $SmZrO_2N$. $RZrO_2N$ (R = Pr, Nd, and Sm) compounds have tolerance factors of $t = 0.88-0.89$.[24] These are low but not outside the typical range of $0.85 < t < 1.05$ for ambient pressure perovskites. Thus, while high pressure may play some part in stabilizing the perovskite structure type, its principal role here is to prevent nitrogen loss under reaction conditions.

This study shows that new mixed-metal oxynitrides are accessible by a direct solid-state reaction between metal oxides and oxynitrides at high pressures. The high temperatures needed to promote diffusion of R^{3+} and Zr^{4+} cations would lead to nitrogen loss at ambient pressure, but the application of 2−3 GPa pressure has enabled the $RZrO_2N$ phases to be obtained as majority phases. Unfortunately, the very stable secondary pyrochlore phases also appear to accommodate nitrogen and so are also formed in competition with the perovskite under the investigated high-pressure reaction conditions. Purer samples of the perovskites will be needed to study their physical properties.

In conclusion, this study demonstrates that high-pressure solid-state reactions between accessible metal nitrides or oxynitrides and oxides of metals that are difficult to nitride are viable and may lead to the discovery of many new mixed-metal oxynitrides.

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Supporting Information Available: Powder X-ray diffraction refinements of $RZrO_2N$ (R = Pr, Nd, and Sm) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The tolerance factor for an ABX_3 perovskite is defined as $t = (r_A + r_X)/2^{1/2}(r_B + r_X)$, where r is the ionic radius. The ideal cubic perovskite structure has $t = 1$.