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Powder neutron diffraction of $SrNbO_2N$ at room temperature and 1.5 K

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The structure of strontium niobium dioxygen nitride, $SrNbO_2N$, has been solved by powder neutron diffraction at room temperature and 1.5 K. $SrNbO_2N$ crystallizes in the tetragonal space group *I*4/*mcm*, with $a = 5.7056$ (4) and $c = 8.1002$ (9) Å at room temperature, and $a = 5.6938$ (4) and $c = 8.0974$ (8) Å at 1.5 K. The crystal structure is derived from the cubic perovskite archetype by a slight rotation of the $Nb(O,N)_6$ octahedra with respect to the tetragonal axis. A partially ordered distribution of oxygen and nitrogen on the anionic sites was found.

Comment

Perovskite-related oxides of transition metals with a d^0 configuration (*e.g.* Ti^{4+}, Nb^{5+} or Ta^{5+}) are usually colourless insulators. The corresponding oxynitrides, on the other hand, often exhibit bright colours and a significantly lower resistivity. The origin for this phenomenon lies in the more covalent character of the *M*—N bond compared with the corresponding *M*—O bond, leading to a reduction of the electronic band gap. Their colour and electrical properties make oxynitride perovskites interesting candidates as pigments (Jansen & Letschert, 2000) or as photocatalysts, *e.g.* for the light-induced water-splitting reaction (Kasahara *et al.*, 2002).

Due to their very similar atomic form factors, O and N cannot be distinguished by X-ray diffraction. As an additional disadvantage, X-ray patterns of perovskites are usually dominated by the contribution of heavier elements (*i.e.* the cations), making it difficult to obtain detailed information about the anions. Neutron diffraction, on the other hand, is well suited to the investigation of oxynitride perovskites; O and N differ significantly in their neutron scattering lengths and can therefore be easily distinguished. Additionally, the scattering lengths of oxygen and nitrogen are comparable with those of the cationic species, making it possible to determine the exact positions, (anisotropic) displacement parameters and site-occupation factors of these anions.

On the basis of powder X-ray diffraction measurements, $SrNbO_2N$ was originally reported to possess a cubic perovskite structure (Marchand *et al.*, 1986). Very recently, Kim *et al.* (2004) published a structural model in the correct space group, *I*4/*mcm*. As these authors also used powder X-ray diffraction, no information about the anionic ordering could be provided. Furthermore, the small scattering contribution of the anions makes it impossible to distinguish between space group *I*4/*mcm* and other related space groups, such as $I\bar{4}2m$. Against this background, we present here the crystal structure determination of the title compound, (I), obtained from room- and low-temperature powder neutron diffraction data.

The present neutron diffraction data were recorded on the High-Resolution Powder Diffractometer for Thermal

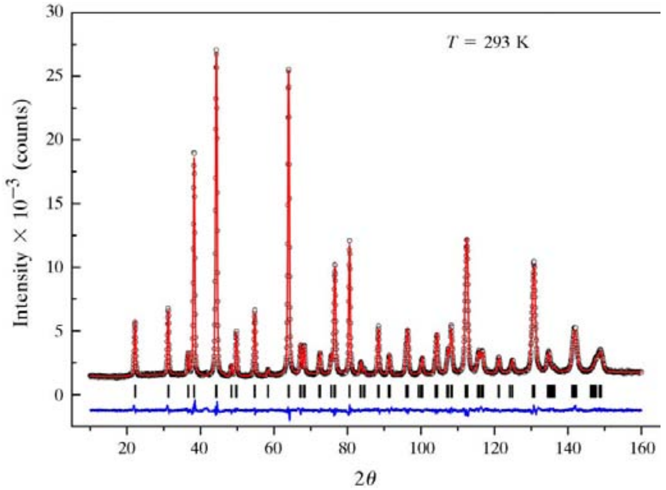

Figure 1
A Rietveld refinement plot for $SrNbO_2N$ at 293 K, showing the observed and difference profiles. The reflection positions are shown above the difference profile.

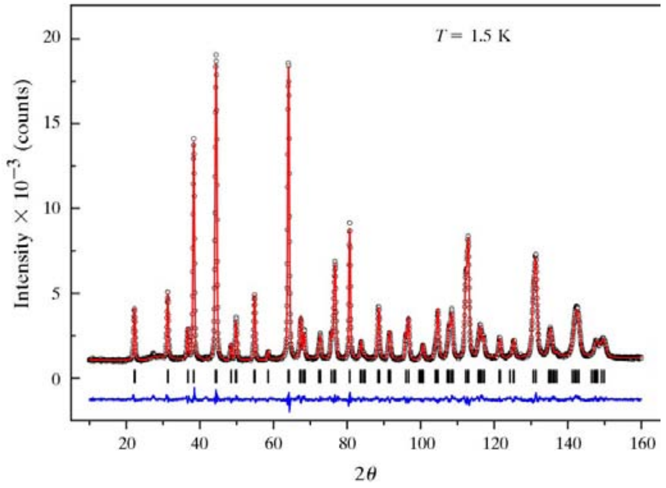

Figure 2
A Rietveld refinement plot for $SrNbO_2N$ at 1.5 K, showing the observed and difference profiles. The reflection positions are shown above the difference profile.

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Neutrons (HRPT) of the Swiss Neutron Spallation Source (SINQ) at the Paul Scherrer Institute (PSI) in Switzerland. Data collection was performed in the high-intensity mode of the instrument.

The powder neutron patterns for the measurements at 293 and 1.5 K, together with the fit results and their differences, are shown in Figs. 1 and 2. All peaks could be indexed with a tetragonal unit cell, with $a = b \simeq a_c^{1/2}$ and $c \simeq 2a_c$ (a_c is the cell parameter of the cubic perovskite). It is to be noted that, although $2^{1/2}a \simeq c$ (with differences of only −0.031 Å at 293 K and −0.045 Å at 1.5 K), the unit cell is not cubic. Using a LeBail fit of the neutron data with the corresponding *F*-centred cubic supercell, only a poor agreement was achieved. Additionally, the powder X-ray pattern showed a pronounced splitting of various peaks, clearly proving the tetragonal distortion.

As a starting model for the refinement of (I), the structure of $SrTaO_2N$ (Günther *et al.*, 2000) was used. Other structural models found for related oxynitride perovskites, such as $CaTaO_2N$ and $LaTaON_2$ (Günther *et al.*, 2000) and $LaTiO_2N$ (Clarke, Guinot *et al.*, 2002), were also considered, but led to rather poor agreements. Since Pors *et al.* (1988) reported $SrTaO_2N$ to crystallize in space group $I\bar{4}2m$, we additionally attempted to refine our neutron data in this space group, which indeed led to reasonable results. The residual parameters, on the other hand, remained slightly larger than those for the calculations in *I*4/*mcm*, despite the greater number of refinable parameters. For this reason, we concluded that the higher symmetric space group *I*4/*mcm* is better suited to describe the structure of $SrNbO_2N$.

Refinement runs converged smoothly, yielding the results listed below. To reduce the number of free parameters, isotropic displacement parameters were used for Sr and Nb. This approximation is reasonable because, in perovskites, the displacements of the cations are known to be usually almost spherical. Rietveld programs tend to underestimate heavily the errors of the cell parameters. For this reason, we multiplied the standard uncertainties of *a* and *c* by a factor of 10.

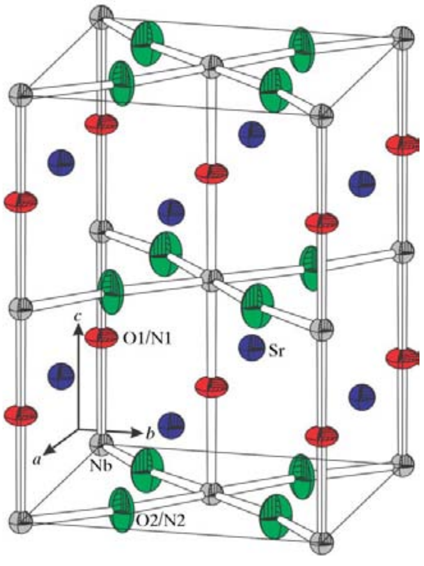

Figure 3
The structure of $SrNbO_2N$ at 293 K. Displacement parameters are shown at the 90% probability level.

A graphical presentation of the crystal structure of (I) at 293 K is shown in Fig. 3. Surprisingly, the structure barely changes upon cooling. While the cell parameter *a* decreases by only 0.2%, *c* remains almost unchanged ($\Delta c/c = -0.03\%$). In addition, the Nb—O/N distances remain very similar. As can be seen in Fig. 3, the $Nb(O,N)_6$ octahedra are slightly rotated around the crystallographic *c* axis. The rotation angle increases from 5.5 (1) to 6.6 (1)° on cooling to 1.5 K.

The experimentally determined nitrogen contents of 0.93 (3) and 0.96 (3) at 293 and 1.5 K, respectively, are (within a 2σ tolerance range) in good agreement with the expected value of 1. Comparing the O/N distribution, we observed a partial order of the anions. The axial position (4*a*) is occupied by 84% O and 16% N, while for the equatorial position (8*h*), an occupancy of 61% O and 39% N was obtained. Within experimental error, identical values were found for the room- and low-temperature measurements. It is interesting to compare these data with the results given for the closely related oxynitride $SrTaO_2N$. In contrast with the oxygen enrichment on the axial position which we have observed in $SrNbO_2N$, Pors *et al.* (1988) and Clarke, Hardstone *et al.* (2002) reported a slight enrichment of oxygen on the equatorial position. Günther *et al.* (2000), on the other hand, found complete O/N order, with the O ions exclusively occupying the equatorial sites. It was assumed that the different results for $SrTaO_2N$ originate from variations in sample preparation. Further investigations are currently in progress to study the influence of the preparation technique on anionic order in $SrNbO_2N$.

Experimental

Polycrystalline $SrNbO_2N$ was prepared by ammonolysis of thoroughly ground stoichiometric mixtures of $SrCO_3$ and Nb_2O_5 in alumina boats at 1223 K. An equimolar amount of KCl was added as mineralizer. Phase purity was checked by X-ray diffraction measurements. A single-phase product was achieved after two ammonolysis cycles of 18 h each with an intermediate regrinding.

Compound (I) at 293 K

Crystal data

$SrNbO_2N$
$M_r = 906.72$
Tetragonal, *I*4/*mcm*
$a = 5.7056$ (4) Å
$c = 8.1002$ (9) Å
$V = 263.69$ (4) Å^3
$Z = 1$
$D_x = 5.710$ Mg m^{-3}

Neutron radiation
$\lambda = 1.4933$ Å
$\mu = 0.01$ mm^{-1}
$T = 293.1$ (2) K
Irregular, brown
Specimen shape: cylinder
50 × 10 mm

Table 1
Selected geometric parameters (Å, °) for (I) at 293 K.

Nb—O1/N1	2.0250 (2)	Sr—O1/N1	2.8528 (2)
Nb—O2/N2^{i}	2.0266 (8)	Sr—O2/N2^{ii}	2.9990 (6)
Sr—O2/N2^{i}	2.7244 (5)		
Nb^{iii}—O2/N2—Nb^{iv}	169.0 (1)		

Symmetry codes: (i) $x-1, y, z$; (ii) $-y, x, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iv) $1+x, y, z$.

Data collection

SINQ HRPT diffractometer
PSI, Villigen, Switzerland
Specimen mounting: vanadium can
Specimen mounted in transmission mode
98 measured reflections
98 independent reflections
θ_{max} = 74.5°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 10$
$2\theta_{min}$ = 4.55, $2\theta_{max}$ = 164.80°
Increment in 2θ = 0.050°

Refinement

Refinement on I_{net}
R_p = 0.0253
R_{wp} = 0.0327
R_{exp} = 0.0200
S = 1.63
$2\theta_{min}$ = 10, $2\theta_{max}$ = 155°
Increment in 2θ = 0.05°
Wavelength of incident radiation: 1.4933 Å
Profile function: Thompson–Cox–Hastings pseudo-Voigt
98 reflections
20 parameters
$(\Delta/\sigma)_{max} < 0.001$

Compound (I) at 1.5 K

Crystal data

$SrNbO_2N$
M_r = 906.48
Tetragonal, $I4/mcm$
a = 5.6938 (4) Å
c = 8.0974 (8) Å
V = 262.51 (4) Å^3
Z = 1
D_x = 5.734 Mg m^{-3}
Neutron radiation
λ = 1.4933 Å
μ = 0.01 mm^{-1}
T = 1.53 (2) K
Irregular powder, brown
Specimen shape: cylinder
50 × 10 mm

Data collection

SINQ HRPT diffractometer
PSI, Villigen, Switzerland
Specimen mounting: vanadium can
Specimen mounted in transmission mode
98 measured reflections
98 independent reflections
θ_{max} = 74.9°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 10$
$2\theta_{min}$ = 4.55, $2\theta_{max}$ = 164.80°
Increment in 2θ = 0.050°

Refinement

Refinement on I_{net}
R_p = 0.0284
R_{wp} = 0.0363
R_{exp} = 0.0232
S = 1.57
$2\theta_{min}$ = 10, $2\theta_{max}$ = 160°
Increment in 2θ = 0.05°
Wavelength of incident radiation: 1.4933 Å
Profile function: Thompson–Cox–Hastings pseudo-Voigt
98 reflections
20 parameters
$(\Delta/\sigma)_{max} < 0.001$

For both anion positions, a complete site occupation was assumed and only the ratios O1:N1 and O2:N2 were allowed to vary.

For both experiments, data collection: *SINQ Instrument Control System* (*SICS*) (Fischer *et al.*, 2000); cell refinement: *FULLPROF*2000 (Rodríguez-Carvajal, 1990); data reduction: *SINQ Instrument Control System* (*SICS*); program(s) used to refine structure: *FULLPROF*2000; molecular graphics: *ATOMS* (Dowty, 1995); software used to prepare material for publication: *FULLPROF* 2000 and *PLATON* (Spek, 2003).

Table 2
Selected geometric parameters (Å, °) for (I) at 1.5 K.

Nb—O1/N1	2.0243 (2)	Sr—O1/N1	2.8469 (2)
Nb—O2/N2^{i}	2.0263 (6)	Sr—O2/N2^{ii}	3.0227 (5)
Sr—O2/N2^{i}	2.6965 (4)		
Nb^{iii}—O2/N2—Nb^{iv}	166.9 (1)		

Symmetry codes: (i) $x-1, y, z$; (ii) $-y, x, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iv) $1+x, y, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1729). Services for accessing these data are described at the back of the journal.

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