Crystal Structure Determination of the Oxynitride Sr$_2$TaO$_3$N

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The crystal structure of the strontium tantalum oxynitride Sr$_2$TaO$_3$N has been resolved by Rietveld refinement using time-of-flight neutron powder diffraction data. The structure is of the K$_2$NiF$_4$ type with a partially ordered anion sublattice (tetragonal, $I4/mmm$, $a = 4.04127(3)$ Å, $c = 12.6073(2)$ Å, $c/a = 3.120$, $Z = 2$). The tantalum atoms are at the center of TaO$_2$(O, N)$_4$ octahedra built up from two oxygen atoms at the apexes and four (N + O) atoms statistically forming the median plane. The strontium atoms have a coordination number of nine: SrO$_5$(O, N)$_4$. The profile agreement factors are $R_p = 0.022$, $R_{wp} = 0.016$, $R_{exp} = 0.012$, and $R_I = 0.063$.   © 1999 Academic Press

Key Words: Sr$_2$TaO$_3$N, K$_2$NiF$_4$ structure; time-of-flight neutron diffraction; oxynitride.

INTRODUCTION

Many oxynitrides can be considered to be offspring of oxide parents in which some of the oxygen has been replaced by nitrogen. In certain cases, it is possible to find corresponding oxide compositions, with the same general stoichiometry, from which they are derived by applying the cross-substitution principle. This principle consists of compensating, from a charge balance viewpoint, the anionic substitution of trivalent nitrogen for divalent oxygen by an equivalent cationic substitution. Oxynitrides will be able to have the same structure type as parent oxides provided that the substituting cations are compatible in size. This principle has been widely used to prepare new oxynitrides of the predicted structure type (1, 2). Besides this same general chemical role as oxygen played by nitrogen, an important question arises about the precise location of the nitrogen atoms and their role in the structural arrangement. Neutron diffraction is essential here, as the X-ray scattering factors of oxygen and nitrogen are not sufficiently different to permit the two atoms to be distinguished. In contrast, the neutron scattering length of nitrogen, 0.94×10^{-12} cm, is significantly larger than that of oxygen, 0.575×10^{-12} cm, thus making it possible to determine whether the anion sublattice is ordered.

Among the oxynitrides studied by neutron diffraction, only a few have been shown to exhibit an ordered nitrogen/oxygen arrangement. That is the case, for example, in TaON (3) with the ZrO$_2$ Baddeleyite-type structure and in Nd$_2$AlO$_3$N (4) with the K$_2$NiF$_4$-type structure. In this paper, another K$_2$NiF$_4$-type oxynitride has been studied by neutron diffraction, in which only partial ordering is encountered.

EXPERIMENTAL

Oxynitrides A_2TaO$_3$N (A = Ca, Sr, Ba) have been obtained by reaction between ammonia and an appropriate stoichiometric mixture (atomic ratio A/Ta = 2) of alkaline-earth carbonate and tantalum oxide at 900–1000°C, as described previously (5). The strontium compound is an orange-colored powder which was prepared in a pure state, as verified by X-ray diffraction, after several 15-h heating cycles in flowing ammonia with subsequent regrinding in alcohol in an agat mortar. No other strontium and/or tantalum compounds were detected, thus confirming the product obtained was stoichiometric with respect to the metals. Chemical analysis of nitrogen was measured as N$_2$ by thermal conductivity with a LECO analyzer previously calibrated with pure 99.995% N$_2$ gas. This analysis confirmed the Sr$_2$TaO$_3$N formulation (N wt% calc: 3.35; N wt% exp: 3.5(2)).

Time-of-flight (TOF) neutron powder diffraction experiments were performed using the medium resolution diffractometer Polaris at the ISIS spallation source. The Sr$_2$TaO$_3$N powder was placed in a 5-mm diameter vanadium sample holder. Data were collected over a TOF range from 2400 to 19000 μs (*d* spacings range = 0.5–3.1 Å; constant resolution $\Delta d/d \sim 5.10^{-3}$) with a bank of ^{3}He ionization counters situated at a diffraction angle of

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$2\theta = 145°$ in a back scattering geometry (6). The acquisition time was on the order of 4 h. The temperature was controlled at 18°C during acquisition. The data collected were normalized for the incident flux profile measured using the scattering from a vanadium sample and Rietveld profile refinements were performed using the computer program TF12LS (7). All figures in parentheses refer to standard deviations given by TF12LS.

RESULTS AND DISCUSSION

The A_2BX_4 compounds with the tetragonal K_2NiF_4 structure, space group $I4/mmm$, $Z = 2$, can be described as two-dimensional perovskites (8). This structure consists of layers of corner-sharing BX_6 octahedra interspaced by A^{n+} cations. The coordination number of the A cations is nine instead of twelve in the cubic ABX_3 perovskite structure.

The oxynitride Sr_2TaO_3N crystallizes with this structure and the following refined unit cell parameter values at 18°C have been obtained:

$$a = 4.04127(3) \text{ Å}$$
$$c/a = 3.120$$
$$c = 12.6073(2) \text{ Å}$$

The observed systematic absences are consistent with the space groups $I4/mmm$ and $I4mm$ depending on whether the anion sublattice is disordered or ordered, respectively. In a first step, we tried to refine the structure in the $I4mm$ space group permitting an ordered arrangement, with nitrogen and oxygen atoms respectively distributed in $2a$ and $(2a + 4b)$ positions. The calculations did not lead to satisfactory results: $\chi^2 = 3.7$, anomalously high values of temperature factors, and indications of correlations between O and N coordinates of the $2a$ positions. Thus, in a second step the anions were put randomly in $4c$ and $4e$ positions of the centrosymmetric $I4/mmm$ space group: the fit was better, with χ^2 equal to 2.1. However, a few of the intensities were not well fitted, suggesting that nitrogen was preferentially located in the special position $4c$ $(0, 1/2, 0)$. A calculation based on this hypothesis led to a χ^2 value of 1.8. The scale factor, background, unit cell parameters, isotropic atomic displacement parameters, and $z(Sr)$ and $z(O2, N2)$ coordinates were varied simultaneously in the final refinement. The crystallographic details are gathered in Table 1, and the observed and calculated powder neutron diffraction profiles are displayed in Fig. 1.

The final atomic position parameters, occupancy and isotropic atomic displacement parameters are given in Table 2.

In conclusion, although a partial ordering occurs in the anion sublattice of Sr_2TaO_3N, the space group remains $I4/mmm$. Figure 2 shows the corresponding unit cell. The structural arrangement consists of layers of corner-sharing

TABLE 1

Space group	$I4/mmm$
Z	2
a	4.04127(3)
c	12.6073(2)
Diffraction angle	145°
d-spacings range	0.5–3.1 Å
No. of observations	3381
No. of reflections	588
No. of variables	24
χ^2	1.81
R_p	0.022
R_{wp}	0.016
R_{exp}	0.012
R_I	0.063

$TaO_2(O, N)_4$ octahedra, apical sites being occupied primarily by oxygen (93%) and median sites by oxygen and nitrogen. The strontium atoms lie between the layers. The bond lengths in the coordination polyhedra of the strontium and tantalum atoms are reported in Table 3.

A large number of oxides and fluorides adopt the K_2NiF_4 structure. In the case of the oxides, numerous examples are known with two different cations A and A', yielding the formula $AA'BO_4$ (9). In contrast, very few compounds with two anions have been isolated. These are limited to the oxyfluorides K_2NbO_3F (10) and Sr_2FeO_3F (11) and the oxynitrides R_2AlO_3N ($R = La \rightarrow Eu$) (12, 13) and A_2TaO_3N (A = alkaline-earth element) (5).

As mentioned earlier, an ordered arrangement between oxygen and nitrogen was observed in Nd_2AlO_3N (4),
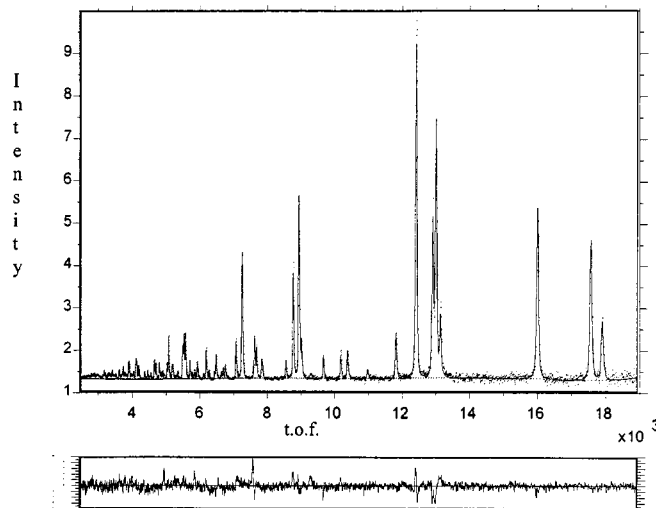

FIG. 1. Experimental (dotted line) and calculated (solid line) neutron time-of-flight (TOF) powder diffraction profiles from the final Rietveld refinement of Sr_2TaO_3N. Intensity is in arbitrary units and the difference/esd profile is also given.

TABLE 2

Atom	Position	Atomic position paramers	Occupancy	B (Å^2)
Ta	$2a$	0 0 0	1	0.29(2)
Sr	$4e$	0 0 0.3546(1)	1	0.56(2)
O1	$4c$	0 0.5 0	0.57(1)	0.53(2)
N1	$4c$	0 0.5 0	0.43(1)	0.53(2)
O2	$4e$	0 0 0.1602(2)	0.93(1)	1.25(4)
N2	$4e$	0 0 0.1602(2)	0.07(1)	1.25(4)

TABLE 3

Sr–(O1, N1)	×4	2.728(1)
Sr–(O2, N2)	×4	2.864(1)
Sr–(O2, N2)	×4	2.451(1)
Ta–(O1, N1)	×4	2.021(1)
Ta–(O2, N2)	×4	2.020(1)

resulting in AlO_5N octahedra in which one apex is occupied by the nitrogen atom. This difference with respect to Sr_2TaO_3N is also revealed by their thermal expansion coefficients. Whereas Nd_2AlO_3N exhibits a strong anisotropic character, $\alpha_a = 0.51 \cdot 10^{-5}\,K^{-1}$, $\alpha_c = 3.08 \cdot 10^{-5}\,K^{-1}$ (14), a lesser anisotropy is observed for Sr_2TaO_3N: $\alpha_a = 0.99 \cdot 10^{-5}\,K^{-1}$, $\alpha_c = 1.46 \cdot 10^{-5}\,K^{-1}$ (14). However, in comparison, for K_2NiF_4-type monoanionic compounds such as K_2NiF_4 itself or Sr_2TiO_4, the thermal expansion along the tetragonal $\mathbf{a}$ and $\mathbf{c}$ directions is very similar (10):

$$K_2NiF_4 : \alpha_a = 2.87 \cdot 10^{-5}\,K^{-1}, \ \alpha_c = 2.91 \cdot 10^{-5}\,K^{-1},$$

$$Sr_2TiO_4 : \alpha_a = 1.46 \cdot 10^{-5}\,K^{-1}, \ \alpha_c = 1.44 \cdot 10^{-5}\,K^{-1}.$$
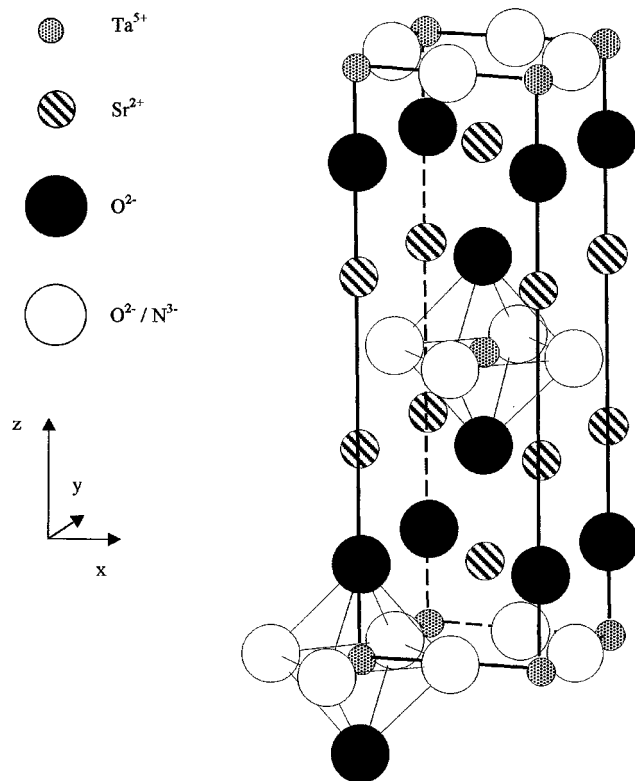
FIG. 2. Perspective view of the Sr_2TaO_3N unit cell.

Therefore, the intermediate situation encountered with Sr_2TaO_3N is in agreement with the partially ordered anionic arrangement observed.

In the K_2NiF_4-type A_2BX_4 compounds, the value of the c/a unit cell parameter ratio, calculated assuming regular contacts between atoms, is equal to 3.414 $(2 + \sqrt{2})$ (5). In fact, the experimental c/a values are often lower, for example 3.264 in K_2NiF_4 or 3.244 in Sr_2TiO_4. In Sr_2TaO_3N, this value is found to be even lower: $c/a = 3.120$. In contrast, Nd_2AlO_3N shows a c/a ratio of 3.382, which is very close to the ideal value. This is due in the latter case to the distorsion of the AlO_5N octahedra, elongated along the $\mathbf{c}$ direction (4):

$$Al\text{–}O \ (median) : 1.855(0) \ Å, \ Al\text{–}O \ (apical) : 2.086(8) \ Å,$$

$$Al\text{–}N \ (apical) : 2.130(6) \ Å.$$

In contrast, as can be seen in Table 3, the Ta–O and Ta–(O, N) distances in the TaO_4N_2 octahedra are identical. Let us note that very similar values (Ta–(O, N) = 2.022(2) and 2.021(2) Å) were observed in $SrTaO_2N$, which has a distorted perovskite-type structure in which O and N are randomly distributed (16). The lower value of the c/a ratio in Sr_2TaO_3N with respect to that calculated can be explained by the great differences between the Sr–O distances in the SrO_7N_2 polyhedra. A very short Sr–O distance of 2.451(1) Å is observed along th $\mathbf{c}$ direction as compared to the other distances, in particular to the 2.864(1) Å which separate the strontium atom from the four oxygen located practically in the same xy plane: $z_{Sr} = 0.1454(1)$, $z_O = 0.1602(2)$. In comparison, the calculated Sr–O distances in Sr_2TiO_4 are, respectively, 2.556 Å for the shortest (parallel to $\mathbf{c}$) and 2.748 Å for the four longest (perpendicular to $\mathbf{c}$) ($z_{Sr} = 0.145$, $z_O = 0.152$) (15).

CONCLUSION

The oxynitride Sr_2TaO_3N can be considered as deriving from Sr_2TiO_4 through the cross-substitution $Ta^{+V} + N^{-III} = Ti^{+IV} + O^{-II}$. Both compounds belong to the same K_2NiF_4 structure type, with nitrogen and oxygen being partially ordered in Sr_2TaO_3N.

The fact that nitrogen is less electronegative than oxygen leads to more covalent bonding in nitrides and oxynitrides than in oxides. Substitution of nitrogen for oxygen modifies

the band structure and if the highest oxidation state of the transition metal can be stabilized, as is the case for tantalum in Sr_2TaO_3N, it often results in the color of the nitride-type compound being different from that of corresponding oxides. In the present case, it is illustrated by the orange color of the nitrided powder whereas the tantalates are white. This fact can be interpreted as a reduction of the gap between the valence and the conduction band. Knowing the crystal structure of Sr_2TaO_3N, it is now of interest to determine precisely the band structure of this compound in order to further understand the relationship with its color.

ACKNOWLEDGMENTS

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