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(Ba₆O)(ReN₃)₂: Synthesis, crystal structure and physical properties

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Abstract. Reacting a mixture of Ba and Re (3:1) at 850 °C under flowing nitrogen has yielded the nitride-oxide (Ba₆O)(ReN₃)₂ (*R* $\bar{3}$ (No. 148); *a* = 8.1178(2) Å, *c* = 17.5651(4) Å; *V* = 1002.43(5) Å³; *Z* = 6). According to a structure refinement on X-ray powder data, this compound is isostructural to a recently described nitride-oxide of osmium of analogous composition. The structure consists of sheets of trigonal ReN₃ units and trigonal antiprismatic Ba₆O groups. The Ba–O distance of 2.73 Å is close to the sum of the respective ionic radii. The trigonal ReN₃³⁻ nitride anion displays a Re–N bond

length of 1.94 Å, and is planar within the limits of experimental error. The constitution of the anion was confirmed by IR and Raman spectroscopy. The nitride-oxide is stable up to 1000 °C, semiconducting ($\sigma = 4.57 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at RT), and paramagnetic down to 25 K. A Curie-Weiss analysis resulted in a magnetic moment of $\mu = 0.68 \mu_B$ per rhenium atom.

Keywords: Nitrides; Rhenium; Crystal structure; X-ray powder diffraction

Introduction

Recently, we reported on the synthesis and characterization of (Ba₆O)(OsN₃)₂, the first nitridoosmate [1]. It exhibits the peculiarity of containing oxygen, although its incorporation was (originally) not intended. Obviously, a hypothetic nitridoosmate of composition "Ba₃OsN₃" shows an extreme affinity to oxygen, gettering even traces of oxygen from the flow of purified nitrogen. This phenomenon cannot be understood in terms of structural stability since the by ternary transition metal nitrides widely adopted Ba₃FeN₃ type of structure [2] would also provide a well suitable configuration for "Ba₃OsN₃", as is indicated by the fact that the actual structure of (Ba₆O)(OsN₃)₂ is closely related to the former. Extensive quantum mechanical calculations have proven electronic effects to rather be responsible. In order to check if such a phenomenon is unique and restricted to osmium only, we have run similar syntheses for the system Ba/Re/N/O, indeed yielding the isostructural rhenate (Ba₆O)(ReN₃)₂.

Experimental Section

Synthesis

Ba metal (purified by sublimation) and Re metal were mixed in a 3:1 ratio and filled in a pre-dried (treated in vacuum at *T* = 1000 °C) Ta finger tube. The reactants were heated up to *T* = 850 °C in an atmosphere of nitrogen for 50 h. Nitrogen of quality 4.8 was used and standard drying conditions were applied. After 12, 24 and 36 h, the powder sample was re-ground and analyzed via powder X-ray diffraction. Ba₂N was found as intermediate phase. After the repeated treatments, no indications for the presence of Re metal or Ba₂N were given. The sample is a microcrystalline black powder

which hydrolyzes quickly in moist air.

X-ray powder diffraction

X-ray powder diffraction data of (Ba₆O)(ReN₃)₂ were collected at room temperature with a Stoe Stadi-P transmission diffractometer (primary beam Johansson-type Ge monochromator for Mo-K α_1 -radiation, linear PSD) with the sample sealed in a glass capillary of 0.3 mm diameter (Hilgenberg, glass No. 50). The powder pattern was recorded for 20 h in the range from 2-60° 2 θ with a step width of 0.01° 2 θ using a linear position sensitive detector with an opening of approximately 12° 2 θ . Structure determination and refinement was performed using the program TOPAS Version 3.0 (Bruker AXS, 2007). The peak profiles and precise lattice parameters were determined by a LeBail fit [3] using the fundamental parameter approach of TOPAS [4]. Agreement factors (R-values) of the final Rietveld refinement (Figure 1) are listed in Table 1, the coordinates are given in Table 2, and a selection of intra- and inter-molecular distances and angles is given in Table 3. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-419636, the name of the authors, and citation of the paper.

Thermal analysis

Simultaneous DTA/TG/MS (STA 409, Netzsch) was performed on a sample placed in a corundum crucible under flowing argon (100 ml/min) with a heating rate of 10 K/min.

Spectroscopy

Infrared spectroscopy was performed on a FT-IR spectrometer (IFS 113v, Bruker) from 400 cm⁻¹ to 4000 cm⁻¹ with KBr as the solid matrix. For the Raman experiments the powdered sample was filled in a 1.0 mm lithiumborate glass capillary (Hilgenberg, glass No 14). The measurement was performed with an excitation line of 632.817 nm (Labram O10, single grating). The acquisition time was between 5 to 300 sec with a laser power between 0.4 and 0.004 W.

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Electrical conductivity measurement

Measurements were performed on compacted polycrystalline powder pellets (diameter 5 mm, thickness 0.8 mm, pressed with 920 MPa) using the standard four-point technique.

Energy-dispersive X-ray analysis

EDX analysis was performed on a XL30 TMP (Philips Electron Optics GmbH) equipped with an energy-dispersive detector S-UTW(Li) (EDAX). The powder sample was placed on a sample-holder in a glove-box filled with argon. The sample was attached to the machine via a transfer-chamber, providing inert conditions.

Magnetic measurement

Magnetic susceptibilities were measured with a MPMS7 SQUID Magnetometer (Quantum design) between 2 and 300 K. Powder samples were filled in Suprasil quartz glass tubes filled with helium. The data were corrected for the magnetization of the empty sample holder, and for the diamagnetic contributions of the constituent ions by fitting the data according to $\chi_g(\text{korr}) = \chi_g - \chi_0$. χ_0 was obtained by fitting the experimental data $\chi_g = \chi_0 + C_g/(T-\theta)$.

Results and Discussion

The title compound was synthesized by solid-state reaction from elemental barium and rhenium under flowing nitrogen gas. The detailed mechanism of its formation is unknown, but Ba_2N has been proven to be an intermediate which got consumed in the course of repeated grinding and annealing cycles. EDX analysis on the black microcrystalline powder confirmed the Ba:Re ratio of 3:1, and proved the presence of N and O. The Raman data of the title compound is in good agreement with the data provided for Na_4ReN_3 [5]. Our spectrum comprised nearly the same bands but also some additional ones, not mentioned previously [positions in cm^{-1} : 184, 225, 362, 427, 859, 949, 994]. The strong signal at 949 cm^{-1} is indicative for Re-N multiple bonds. The IR spectrum showed two strong absorptions at 847 cm^{-1} and 650 cm^{-1} (shoulder) which are characteristic for a trigonal-planar ReN_3 group. Similar IR spectra have been reported for $(\text{Ba}_6\text{O})(\text{OsN}_3)_2$ [1] and Ba_3FeN_3 [2]. No indications for N-H or O-H vibrations were noticeable.

Under argon, the compound is stable up to $T = 1000 \text{ }^\circ\text{C}$ (mass loss < 0.5 %), as seen from TG analysis. Massive decomposition starts at $T > 1050 \text{ }^\circ\text{C}$, and up to $T = 1300 \text{ }^\circ\text{C}$ a total mass loss of 3.7 % is recorded. BaO, elemental Re, and Ba_2N were identified as solid residues by X-ray powder diffraction.

The X-ray powder pattern of the compound (Figure 1) was found to be similar to the one of previously described $(\text{Ba}_6\text{O})(\text{OsN}_3)_2$, and both compounds proved to be isostructural. Relevant data concerning the crystal structure is found in tables 1-3. The structure is sketched in Figure 2. The constitutional building blocks are the trigonal antiprismatic Ba_6O group and the trigonal planar ReN_3 moiety. The Ba-O distance is 2.75 \AA , the Ba-Ba distances of the Ba_6 unit are split in a longer (4.03 \AA) and a shorter (3.70 \AA) one. These two different sets of distances are commonly observed in related trigonal antiprismatic Ba_6N groups and were also found in $(\text{Ba}_6\text{O})(\text{OsN}_3)_2$. They are indicative for a filled Ba_6 cluster. Concerning the ReN_3 building block, the Re-N distance is 1.91 \AA , the N-Re-N angle is found to be 120° . These units are packed in ABC sequence with a shift of $2/3 \ 1/3 \ 1/3$ in each step.

The Curie-Weiss law applies in the range from $T = 350 \text{ K}$ down to $T = 25 \text{ K}$. The Weiss constant is $\theta = -16 \text{ K}$. The obtained magnetic moment $\mu = 0.68 \mu_B$ is small, indicating significant spin-orbit coupling.

The title compound is a semiconductor. At temperatures $T < 100 \text{ K}$, the material is insulating with the resistivity ρ exceeding $1.0 \cdot 10^6 \ \Omega$, while the specific conductance at RT is $\sigma = 4.57 \cdot 10^{-3} \ \Omega^{-1}\text{cm}^{-1}$. Applying the Arrhenius model from $T = 100 \text{ K}$ up to 300 K , has yielded an activation energy of $E_a = 0.016 \text{ eV}$. This low value is in accordance with the black colour of the material.

This result is suggesting that the incorporation of oxygen cannot be accounted for by discussing VEC's. We rather regard the capability of osmium and rhenium to adopt higher oxidation states the reason. This is an indispensable precondition for including additional anions, which is not fulfilled by e.g. iron.

Table 1. Crystallographic data for $(\text{Ba}_6\text{O})(\text{ReN}_3)_2$

	$(\text{Ba}_6\text{O})(\text{ReN}_3)_2$
Space group	$R\bar{3}$ (No. 148)
Cell parameters / \AA	$a = 8.1178(2)$ $c = 17.5651(4)$
Cell volume / \AA^3	1002.43(5)
Z	6
T / K	300
Formula weight / g/mol	1296.49
$\rho_{\text{calc}} / \text{g/cm}^3$	5.85
Radiation source/ λ / \AA	0.7093000
Capillary diameter / mm	0.3
$R_{\text{exp}} / \%$ ^[a]	1.44
$R_{\text{wp}} / \%$ ^[a]	4.52
$R_p / \%$ ^[a]	3.92
$R_{\text{bragg}} / \%$ ^[a]	1.93
GoF	3.14

a) as defined in TOPAS [3]

Table 2. Atomic positions and isotropic thermal parameter of $(\text{Ba}_6\text{O})(\text{ReN}_3)_2$

Atom	Wyck.	x/a	y/b	z/c	B / \AA^2
Ba	18f	0.3210(3)	0.2313(2)	0.4180(3)	0.3(3)
Re	6c	0	0	0.2494(4)	0.3(3)
N	18f	0.249(2)	0.217(2)	0.2494(4)	0.3(3)
O	3b	0	0	1/2	0.3(3)

Table 3. Selected bond lengths (\AA) and angles ($^\circ$) for $(\text{Ba}_6\text{O})(\text{ReN}_3)_2$

Re-N	1.91(2)
Re-Ba	3.485(1)
	3.767(6)
	3.822(6)
Ba-N	2.76(2)
	2.85(1)
	3.01(1)
	3.08(1)
	3.20(2)
Ba-O	2.738(3)
Ba-Ba	3.703(6)
	3.885(6)
	4.033(3)
N-Os-N	120.0

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6 We thank A. Schulz, E. Brücher and G. Siegle for measuring the Raman, the
7 magnetic and the conductivity data. Support by the Fonds der Chemischen
8 Industrie (FCI) and the German National Merit Foundation (scholarships for
9 C.L. Schmidt) is gratefully acknowledged.

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25 **Figure 1.** Rietveld plot of $(\text{Ba}_6\text{O})(\text{ReN}_3)_2$.
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28 **Figure 2.** The building blocks ($[\text{Ba}_6\text{O}]^{10+}$ trigonal antiprisms and trigonal pyramidal
29 ReN_3^{5-} anions) are packed in ABC sequence with a shift of $2/3$ $1/3$ $1/3$ each (Re dark
30 green, Ba light green, N blue, O red). The empty trigonal antiprisms from layer to layer
31 formed by six Ba atoms are drawn in transparent grey.
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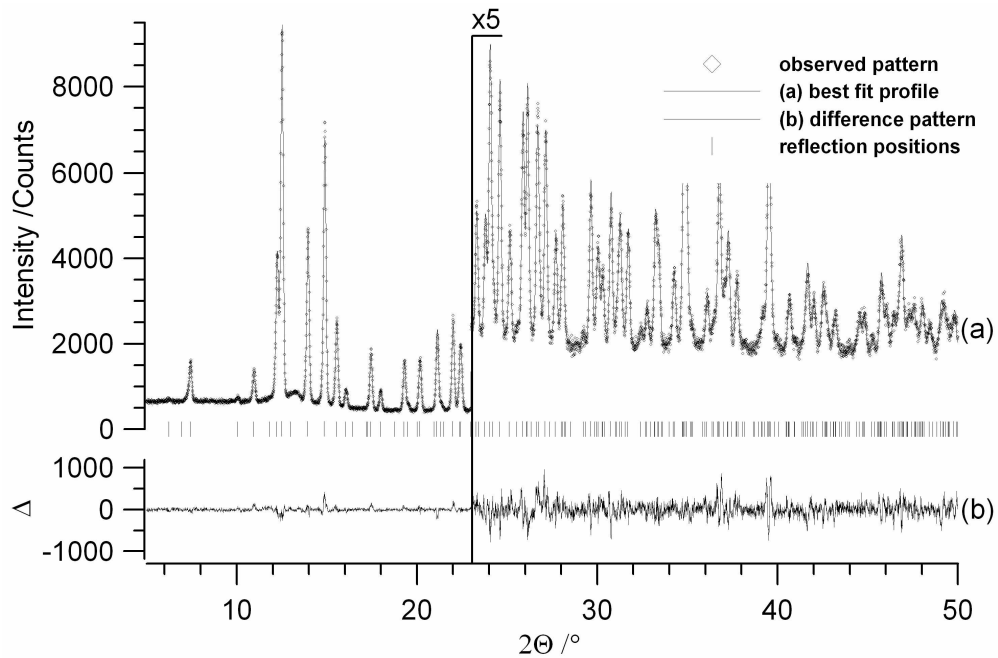


Figure 1. Rietveld plot of $(\text{Ba}_6\text{O})(\text{ReN}_3)_2$
250x164mm (300 x 300 DPI)

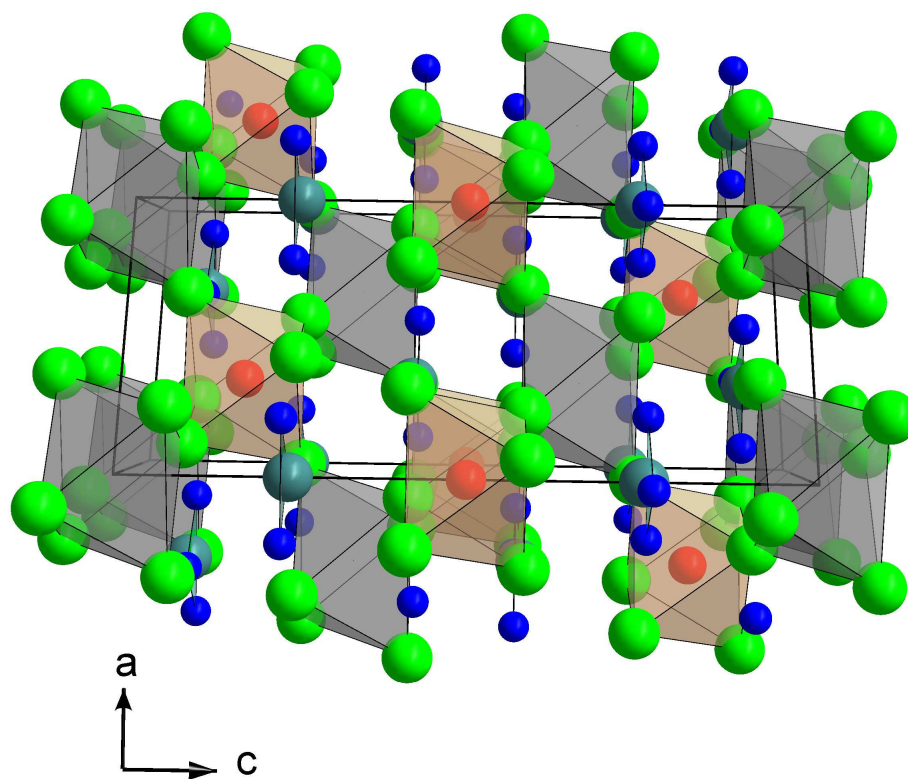


Figure 2. The building blocks ($[\text{Ba}_6\text{O}]^{10+}$ trigonal antiprisms and trigonal pyramidal ReN_3^{5-} anions) are packed in ABC sequence with a shift of $2/3$ $1/3$ $1/3$ each (Re dark green, Ba light green, N blue, O red). The empty trigonal antiprisms from layer to layer formed by six Ba atoms are drawn in transparent grey.
661x661mm (96 x 96 DPI)