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Synthesis and crystal structure of a new oxynitride, Ba_3ZnN_2O

Hisanori Yamane[1], Francis J. DiSalvo*

Department of Chemistry, Cornell University, Ithaca, NY 14853, USA

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Abstract

A new oxynitride, Ba_3ZnN_2O, was prepared as single crystals by slow cooling from 750°C using a starting mixture of Ba, ZnO, NaN_3 and Na. The NaN_3 and Na were respectively the nitrogen source and flux for the crystal growth. The structure was determined by single crystal X-ray diffraction and is tetragonal, space group $P4/mmm$ with $Z = 1$, $a = 4.088(1)$, $c = 9.272(2)$ Å, and $R1 = 0.0288$. The structure is composed of $\{Ba_2ZnN_2\}$ units and $\{BaO\}$ layers. The zinc atom is linearly coordinated by two nitrogen atoms to form a nitridometallate anion, $[N{=}Zn{=}N]^{4-}$, as in Ba_2ZnN_2.

Keywords: Barium zinc oxynitride; Single crystal; Na flux; Crystal structure

1. Introduction

Some new ternary nitrides prepared in recent years consist of nitridometallate anions, such as $[ZnN_2]^{4-}$ in Ca_2ZnN_2 [1], $[FeN_2]^{4-}$ in $Li_4[FeN_2]$ [2], $[GaN_3]^{6-}$ in Ca_6GaN_4 [3] and $[VN_3]^{6-}$ in Ca_3VN_3 [4]. The ionic groups are isosteric with CO_2 or $[CO_3]^{2-}$. Recently, we obtained single crystals of Sr_2ZnN_2 and Ba_2ZnN_2 from metal sources using Na and NaN_3 as a flux and a nitrogen source [5]. These compounds are isostructural with Ca_2ZnN_2 and contain the linear $[ZnN_2]^{4-}$ anions. In the present study, we found a new oxynitride, Ba_3ZnN_2O, which also has linear anion groups in its crystal structure. The present paper describes the synthesis of Ba_3ZnN_2O single crystals and the crystal structure determined by single crystal X-ray diffraction analysis.

2. Experimental

All manipulations were carried out in an Ar-filled glove box. Ba (Aldrich, 99% purity), ZnO (Puratronic JMC), NaN_3 (Aldrich, 99.9% purity) and Na (Strem Chemicals Inc., 99.9% purity) were used as starting materials. Ba 247 mg (1.8 mmol), ZnO 49 mg (0.6 mmol), NaN_3 78 mg (1.2 mmol) and Na 55.2 mg (2.4 mmol) were sealed with an arc furnace under 1 atm of Ar in a Nb tube (8 mm in diameter, 120 mm in length), which in turn was sealed in an evacuated quartz tube. The starting materials were heated at 750°C for 1 h and cooled with a rate of 6.4°C h^{-1}. Single crystals were produced in high yield and were isolated by washing the products in the Nb tube with liquid NH_3 in an inert atmosphere as detailed previously [5]. The Ba:Zn atomic ratio in the single crystals was analyzed by energy dispersive X-ray spectroscopy (EDX) on a scanning electron microscope (JEOL 733).

Precession photographs taken with the crystal sealed in a glass capillary showed that the crystal had tetragonal symmetry. No systematic extinctions were observed. Intensity data were collected on a Syntex P3 four circle diffractometer using Mo Kα radiation and a graphite monochromator. Lattice parameters were obtained from a least squares refinement using the angles of reflections around $\theta = 25°$. Parameters of the data collection and crystallographic data are summarized in Table 1. An empirical absorption correction, based upon a Ψ-scan, was applied using the program XEMP [6].

Since no systematic extinctions were observed, nine tetragonal space groups are possible. We chose the highest symmetry group, $P4/mmm$, and obtained

* Corresponding author.

[1] Current address: Institute for Materials Research, Tohoku University, Sendai 980-77, Japan.

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Table 1
Crystal data and structure refinement for Ba_3ZnN_2O

Empirical formula	Ba_3ZnN_2O
Formula weight	521.41
Diffractometer type	Syntex P3
Monochromator	graphite
Scan type	$\omega - 2\theta$
Temperature	293(2) K
Wavelength	0.71069 Å (Mo Kα)
Crystal system	Tetragonal
Space group	$P4/mmm$ (No. 123)
Unit cell dimensions	$a = 4.088(1)$ Å
	$c = 9.272(2)$ Å
Volume	154.95(6) Å^3
Z	1
Density (calculated)	5.588 Mg m^{-3}
Absorption coefficient	22.511 mm^{-1}
F (000)	220
Crystal size	$0.08 \times 0.12 \times 0.13$ mm^3
θ range for data collection	2.20 to 27.44°
Index ranges	$0 \leq h \leq 5$, $0 \leq k \leq 5$, $0 \leq l \leq 12$
Reflections collected	245
Independent reflections	144 ($R_{int} = 0.0411$)
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	144/0/14
Goodness-of-fit on F^2	1.157
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0264$, $wR2 = 0.0606$
R indices (all data)	$R1 = 0.0288$, $wR2 = 0.0623$
Extinction coefficient	0.015(3)
Largest diff. peak and hole	1.360 and −1.178 e Å^{-3}

$R1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (wF_o^2)^2]^{1/2}$, $w = 1/[\sigma(F_o^2)^2 + (0.0259\ P)^2 + 1.13\ P]$ where $P = [\text{Max}\ (F_o^2, 0) + 2F_c^2]/3$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for Ba_3ZnN_2O

Atom	Site	x	y	z	U_{eq}
Ba(1)	1d	1/2	1/2	1/2	23(1)
Ba(2)	2g	0	0	0.2176(1)	19(1)
Zn	1c	1/2	1/2	0	21(1)
N	2h	1/2	1/2	0.2009(15)	28(3)
O	1b	0	0	1/2	34(5)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

excellent R values. The positions of barium and zinc atoms were determined by trial and error. Nitrogen and oxygen atom positions were found from the difference Fourier map. Refinement and an extinction correction were performed using SHELXL-93 [7]. The analytical forms of scattering factors for neutral atoms, as well as correcting for both real and imaginary components of anomalous dispersion, were used as given in the SHELXL-93 software.

3. Results and discussion

The single crystals were less than 0.5 mm in size and had a dark metallic luster. The color of the powdered sample was dark reddish brown. The crystals and

Table 3
Anisotropic displacement parameters (Å$^2 \times 10^3$) for Ba_3ZnN_2O

Atom	U_{11}	U_{22}	U_{33}	$U_{23} = U_{13} = U_{12}$
Ba(1)	25(1)	25(1)	21(1)	0
Ba(2)	19(1)	19(1)	20(1)	0
Zn	21(1)	21(1)	23(1)	0
N	33(5)	33(5)	18(6)	0
O	41(7)	41(7)	20(8)	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \cdots + 2hka^*b^*U_{12}]$.

Table 4
Selected interatomic distances (Å) for Ba_3ZnN_2O

Zn–N	1.863(14) × 2
Zn–Ba(2)	3.525(1) × 8
Ba(1)–N	2.773(14) × 2
Ba(1)–O	2.891(1) × 4
Ba(2)–N	2.895(1) × 4
Ba(2)–O	2.619(1)
Ba(1)–Ba(2)	3.900(1) × 8

powder were sensitive to moisture and hydrolyzed in air to produce NH_3. The Ba:Zn atomic ratio obtained by semi-quantitative EDX analysis was about 3.4:1, which was close to the ideal ratio of 3:1. From the refinement we could locate one Zn, two Ba and three anions of low Z in the unit cell. Assuming +2 oxidation states of Zn and Ba, we surmised the composition to be Ba_3ZnN_2O. This is in fact also consistent with the amount of O in the reaction mixture and the high yield of product. The oxygen in Ba_3ZnN_2O was derived from ZnO in the following reaction:

$$3Ba + ZnO + N_2 \rightarrow Ba_3ZnN_2O$$

The inner pressure of the Nb tube was over 1 atm after heating. No reaction with the inner wall of the Nb tube was apparent by visual inspection. The excess N_2 derived from NaN_3 probably remained with some partial pressure in the tube.

We attempted to prepare the oxynitride using BaO as an oxygen source and Zn metal as a zinc source in a Na flux, keeping the same molar ratio of the starting elements in the Nb tube (Ba:Zn:N:Na = 1.8:0.6:0.6:3.6). However, the products obtained were $Ba_x(O,N)_y$ having a rock salt-type structure and the intermetallic compound of $BaZn_{13}$:

$$2Ba + BaO + Zn + N_2 \rightarrow Ba_x(O,N)_y + 1/13BaZn_{13}$$

We would expect a thermodynamic product to result independent of starting reagents. In this case, it is not clear if the problem is kinetic (i.e. BaO and $Ba_x(O,N)_y$ are refractory and thus have slow diffusion rates at the synthesis temperatures (note the melting point of BaO is 1918°C)), or indeed if the title compound is metastable.

We also tried to prepare an oxynitride for the system Sr–Zn–N–O, but only the following reaction occurred:

$$3Sr + ZnO + N_2 \rightarrow Sr_2ZnN_2 + SrO$$

The apparent inability to form Sr_3ZnN_2O, under the same conditions as those which result in Ba_3ZnN_2O, suggests that the free energy of formation of the Sr oxynitride is not sufficiently negative to overcome the extra free energy of formation of SrO ($\Delta_f G° = -561.9$ kJ mol^{-1}) relative to that of BaO (-525.1 kJ mol^{-1}) [8].

Since electron scattering powers of oxygen and nitrogen are very close, we could not distinguish oxygen from nitrogen in the structure analysis. Thus we assumed that oxygen and nitrogen atoms are ordered and in the sites of 1b and 2h respectively. The final value of $R1$ for all data was 2.9%. The maximum and minimum peaks in the final difference Fourier map, 1.360 and -1.178 e Å^{-3} respectively, are close to the position of Ba atoms. Atomic positions and anisotropic displacement parameters are listed in Tables 2 and 3. Selected interatomic distances are summarized in Table 4.

A model in which oxygen and nitrogen atoms were statistically distributed in the anion sites (statistical model) is also possible. However, the Madelung potentials and energies recommend the ordered model. The Madelung energies per formula unit calculated for the ordered and disordered models using the program EUTAX [9] are -17045.83 kJ mol^{-1} and -16357.68 kJ mol^{-1} respectively. In the disordered model, the N^{3-} and O^{2-} atoms (average charge -2.67) statistically occupy the two anion sites which have different Madelung potentials of +26.595 V and +17.638 V. In contrast, the N^{3-} atoms are in the higher potential anion site of +28.048 V and the O^{2-} atoms are in the lower potential anion site of +15.611 V in the ordered model. Neutron diffraction analysis is needed to determine the distribution of the nitrogen and oxygen atoms.

Fig. 1 illustrates the structure of Ba_3ZnN_2O together with that of Ba_2ZnN_2. The structure of Ba_3ZnN_2O is most easily derived from that of Ba_2ZnN_2 by intercalating a layer of rock salt {BaO} between $\{Ba_2ZnN_2\}$ units. The zinc atom in the $\{Ba_2ZnN_2\}$ unit remains linearly coordinated by nitrogen atoms.

The N–Zn bond length of 1.863(14) Å in $[N{=}Zn{=}N]^{4-}$ of Ba_3ZnN_2O is consistent with the lengths found in alkali-earth zinc nitrides (1.8418 Å in Ca_2ZnN_2 [1], 1.874(15) Å in Sr_2ZnN_2 [5] and 1.842(14) Å in Ba_2ZnN_2 [5]) and also with the N–Fe length of 1.86(1) Å in the $[N{=}Fe{=}N]^{4-}$ of Li_4FeN_2 [2].

The Ba(2) atom of Ba_3ZnN_2O is in a square pyramid composed of an apical oxygen atom and four basal nitrogen atoms. The interatomic distances of Ba(2)–apical O and Ba(2)–basal N are a little shorter than the distances of Ba–apical N (2.653(14) Å) and Ba–basal N (2.942(1) Å) in Ba_2ZnN_2 [5] where the Ba atom is in a nitrogen square pyramid.

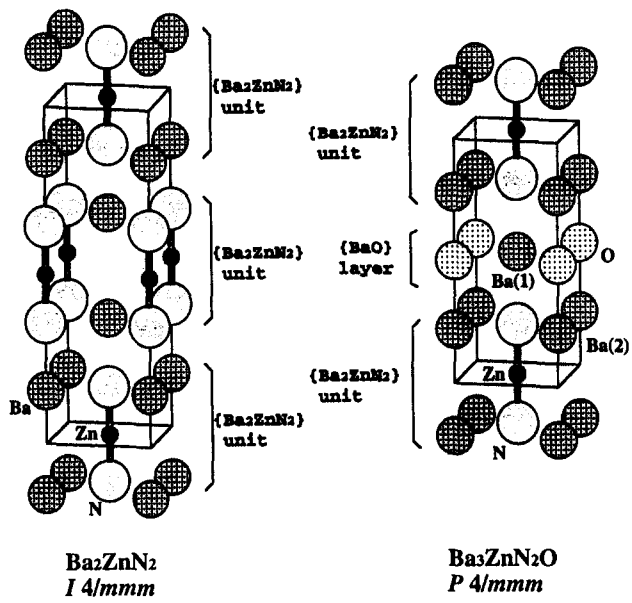

Fig. 1. Structures of Ba_2ZnN_2 and Ba_3ZnN_2O where the bonds in $[N{=}Zn{=}N]^{4-}$ are emphasized.

Ba(1) is octahedrally coordinated by four oxygen atoms in square arrangement (in the a–b plane) with two trans nitrogen atoms (along the c axis). The Ba(1)–O distance almost equals the Ba(2)–N distance. However, as shown in Table 3, the thermal displacement parameters of the oxygen atom in the a–b plane are larger than those of the nitrogen atoms. This might suggest that the oxygen atoms are loosely packed along the a–b plane owing to the smaller O^{2-} ionic

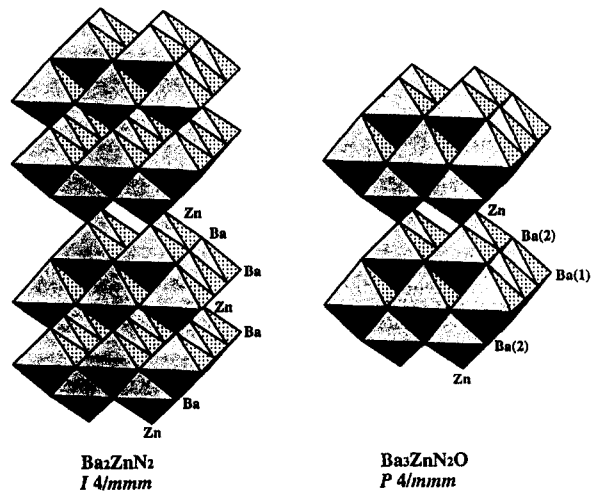

Fig. 2. Structures of Ba_2ZnN_2 and Ba_3ZnN_2O illustrated with nitrogen-centered edge and vertex shared metal octahedra.

radius (1.40 Å) compared with the N^{3-} ionic radius (1.43 Å).

As demonstrated in the structure of Ba_2ZnN_2, the structure of Ba_3ZnN_2O can also be viewed as a stacking of metal octahedra (Fig. 2). In the case of Ba_2ZnN_2, two layers of the nitrogen-centered octahedra are linked by sharing of the apical zinc atoms. The structure of Ba_3ZnN_2O consists of triple octahedral layers linked by sharing of the apical zinc atoms.

To summarize, single crystals of Ba_3ZnN_2O were synthesized by slow cooling from 750°C using Na and NaN_3 as a flux and a nitrogen source respectively. The structure is related to that of Ba_2ZnN_2 and analyzed by single crystal X-ray diffraction assuming a nitrogen–oxygen ordering model. The {Ba–O} layer intervened between the $\{Ba_2ZnN_2\}$ units in which linear $[N{=}Zn{=}N]^{4-}$ groups were included.

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