$NaBa_2O$: A Fresh Perspective in Suboxide Chemistry**

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The 1932 edition of Gmelin's Handbook of Inorganic Chemistry[1] cites several works describing a supposedly metallic suboxide of barium with the composition Ba_2O. This suboxide could, for example, be obtained by treating the metal with BaO at around 1100 °C. In the 1960 complimentary volume on barium[2] the existence of the suboxide is questioned. The solubility of metallic barium in the oxide was cited as a reason for the erroneous reports of Ba_2O. So far no barium suboxides have been reliably characterized.

The chemistry of alkali metal (A) suboxides, on the other hand, was developed in the 1970s[3] following initial reports on cesium suboxides at the beginning of the last century.[4] All of the investigated cesium and rubidium compounds contain oxygen-centered A_6O octahedra of metal atoms that are condensed to larger clusters through face sharing.

The motif of octahedral clusters repeats itself in the still growing family of alkaline earth metal (AE) subnitrides, in which AE_6N clusters or their aggregates form stoichiometric compounds with sodium.[5] The alkali metal suboxides and the alkaline earth metal subnitrides feature a unique combination of ionic bonding within the A_6O or AE_6N clusters and metallic bonding involving the remaining conduction electrons.

Our search for alkaline earth metal suboxides was further stimulated by reports on $M_3Ba_{20}O_5$ (M = Ga, In)[6] and $M_2Ba_{21}O_5$ (M = Si, Ge),[7] which contain $Ba_{18}O_5$ clusters formed by face sharing between five Ba_6O octahedra. These compounds, however, turned out to be oxide hydrides, such as purely ionic $(Ba^{2+})_{21}(Ge^{4-})_2(O^{2-})_5(H^-)_{24}$, when the initially overlooked hydrogen impurity was taken into account.[8, 9]

As Na/K alloy proved to be an excellent flux for the preparation of alkaline earth metal subnitrides, it was also used to prepare a barium suboxide. Additionally, we hoped that a sodium matrix might stabilize the desired suboxide, as in the subnitrides $NaBa_3N$,[13] Na_5Ba_3N,[14] and $Na_{16}Ba_6N$.[15]

First attempts[16] were successful in producing single crystals of a new compound. The crystal structure could be solved and refined based on single-crystal[18] and powder X-ray diffraction data[20] in the stoichiometry $NaBa_2O$,[22] which is the first compound in the Na/Ba/O system.

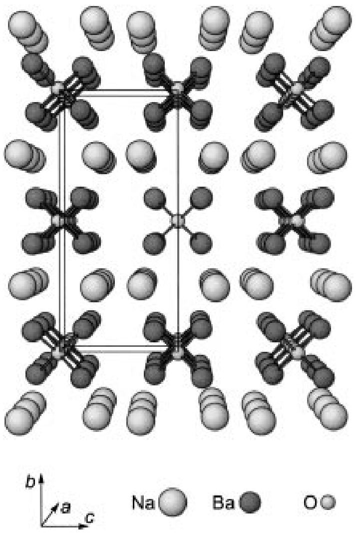

Figure 1. Crystal structure of $NaBa_2O$ as viewed along the linear ${}^{1}_{\infty}[Ba_{4/2}O]$ chains. The orthorhombic unit cell is outlined.

The most striking feature in the crystal structure of $NaBa_2O$ is the presence of Ba_4O tetrahedra instead of the expected Ba_6O octahedra. Edge sharing between the tetrahedra leads to ${}^{1}_{\infty}[Ba_{4/2}O] \cong Ba_2O$ chains, which are stacked parallel to each other and are separated by sodium atoms (Figure 1), resembling the arrangement of Ba_3N chains in $NaBa_3N$[13] and Na_5Ba_3N.[14] Although the ${}^{1}_{\infty}[Ba_{4/2}O]$ chains in $NaBa_2O$ are analogous to the ${}^{1}_{\infty}[SiQ_{4/2}]$ (Q = S, Se) chains in the silicon dichalcogenides,[23] the packing of the ${}^{1}_{\infty}[Ba_{4/2}O]$ chains and Na atoms results in a new structure type. These chains also determine the preferred direction of crystal growth, resulting in needlelike $NaBa_2O$ crystals. The Ba–O distance of 2.5286(3) Å is significantly shorter than that of 2.76 Å in BaO[24] due to the lower coordination numbers CN = 2 and 4 for Ba and O, respectively, in $NaBa_2O$ compared to those in BaO (CN = 6). The separations between the metal atoms are in the range observed in sodium barium subnitrides and are typical for metallic bonding, which is consistent with the formulation $Na^+(Ba^{2+})_2O^{2-} \cdot 3\,e^-$.

The crystal structure of the suboxide can also be described starting from the body-centered cubic (bcc) packing of the metal atoms, as in elemental Na and Ba. In the first step, Ba and Na atoms are arranged in such a way that every third square layer contains Na atoms, with the remaining positions occupied by Ba atoms according to the $MoSi_2$ structure type.[25] In the second step, half of the tetrahedral holes in the remaining Ba double layers are filled in an ordered fashion by O atoms so that the resulting ${}^{1}_{\infty}[Ba_{4/2}O]$ chains run in the [110] direction of the initial bcc lattice (Figure 2). Full occupation of these voids results in a $ThCr_2Si_2$-type structure.[26] Based on this construction, one would expect an ideal a:b:c ratio of $\sqrt{2}$:3:$\sqrt{2}$ (≅1:2.12:1) for $NaBa_2O$, which is within 5 % of the 0.95:2.21:1.00 ratio for the observed lattice constants. Incidentally, the value $c/\sqrt{2} = 4.91$ Å lies between the values for the lattice constants of elemental sodium ($a' = 4.29$ Å) and barium ($a' = 5.02$ Å), suggesting that the above-described construction is realistic.

Surprisingly, the crystal volume of $NaBa_2O$ per formula unit ($V = V_{cell}/Z = 175.2$ Å^3) is larger than the sum $V(Na) + 2\,V(Ba) = 166.3$ Å^3 (Table 1). On first sight it might seem reasonable as the volume of the O atoms adds to that of the metal atoms. However, all suboxides and subnitrides of alkali and alkaline earth metals known so far exhibit crystal volumes

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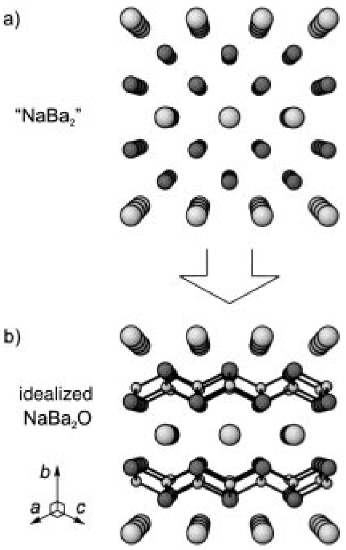

Figure 2. Construction of the crystal structure of $NaBa_2O$ starting from a body-centered cubic lattice as in elemental Na or Ba. Every third layer of the latttice is occupied by Na atoms, with Ba atoms in the remaining layers, corresponding to a hypothetical "$NaBa_2$" alloy (a). The idealized crystal structure of $NaBa_2O$ obtained by filling half of the tetrahedral voids in barium double layers of "$NaBa_2$" by oxygen atoms (b). When this model structure with Ba in (0,0.08333,¼) and Na in (0,¼,¾) is rotated by 45° around the vertical b axis and is allowed to relax, the experimentally observed $NaBa_2O$ structure is obtained (see Figure 1).

Table 1. Crystal volumes per formula unit for several Na/Ba/O compounds. The first four lines are identical to Table 5 in ref. [14].

Material	$V = V_{cell}/Z$ [Å^3]	Volume change[a] [%]	Residual per $BaO_{z/y}$ [Å^3][b]	Ref.
Na	39.5	–	–	[31]
Ba	63.4	–	63.4	[31]
Na_2Ba	142.0	−0.3	63.0	[29]
NaBa	102.8	−0.1	63.3	[28]
$NaBa_2O$	175.2	+5.3	67.9	this work
BaO	42.1	−33.6	42.1	[24]

[a] The procentual volume change for $Na_xBa_yO_z$ is defined as $100 \times [V(Na_xBa_yO_z) - x\,V(Na) - y\,V(Ba)]/[x\,V(Na) + y\,V(Ba)]$. [b] The residual volume for $Na_xBa_yO_z$ is defined as $[V(Na_xBa_yO_z) - xV(Na)]/y$.

corresponding to the sum of the metals, due to dramatic shrinkage of the metal volume upon cation formation. Contractions by $\tfrac{1}{2}V(Cs_2O) - V(Cs) = -66.1$ Å^3 and $V(BaO) - V(Ba) = -21.3$ Å^3 indicate that the addition of O^{2-} ions to the crystal structures cannot overcompensate the volume reduction due to the formation of Cs^+ and Ba^{2+}. However, there exists an additional effect leading to volume expansion in suboxides and subnitrides, namely, coulombic repulsion between the anions and the remaining conduction electrons. This effect can be quantified by the values $V(NaBa_2O) - V(Na) - V(Ba) - V(BaO) = 30.2$ Å^3 and $V(Cs_{11}O_3) - 5\,V(Cs) - 3\,V(Cs_2O) = 83.9$ Å^3, for example, or approximately 30 Å^3 per oxide anion. Such an additional expansion is not enough to overcome the cationic contraction in cesium suboxides ($V(Cs_{11}O_3) = 960.8$ Å^3 is still smaller than $11\,V(Cs) = 1273.7$ Å^3), but suffices in $NaBa_2O$ because the cationic contraction is significantly weaker for barium than for cesium, as mentioned above.

Additional structural and chemical reasons for the large crystal volume of $NaBa_2O$ include 1) the fact that the metal atoms exhibit no close packing and 2) the long Ba–Ba contacts between the $^1_\infty[Ba_{4/2}O]$ chains ($d_{Ba-Ba} \geq 4.959$ Å) leading to electron confinement and expansion as discussed for Ba_3N.[27] The volume of the Wigner–Seitz cell constructed for Na in the intermetallic phases NaBa[28] ($V(Na) = 38.8$ Å^3) and Na_2Ba[29] ($V(Na) = 39.3$ Å^3) is close to that in metallic sodium ($V(Na) = 39.5$ Å^3), whereas it is significantly larger for $NaBa_2O$ ($V(Na) = 46.8$ Å^3). This finding may be associated with the effect described in (2) or even with a polarization toward anionic sodium.[30]

Relatively large crystal volumes of suboxides and subnitrides suggest that these should decompose under pressure, for example according to Equations (1) and (2). We plan to investigate these reactions. In addition, we will attempt to characterize further compounds which, according to preliminary results, appear to exist in the Na/Ba/O system.

$$NaBa_2O \longrightarrow NaBa + BaO \ (\Delta V_1 = -30.3 \text{ Å}^3 \text{ or } -17.3\,\%) \tag{1}$$

$$Cs_{11}O_3 \longrightarrow 5\,Cs + 3\,Cs_2O \ (\Delta V_2 = -83.9 \text{ Å}^3 \text{ or } -8.7\,\%) \tag{2}$$

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[9] It is unclear whether another reported suboxide $Ba_{17}Al_3O_7$,[10] which contains $Ba_{17}Al_2O_7$ clusters also composed of condensed oxygen-centered metal octahedra, is contaminated by hydrogen. Attempts to repeat the synthesis of this compound resulted in preparation of another ionic oxide hydride, $(Ba^{2+})_3Al^{3+}(O^{2-})_4H^-$.[11, 12]

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[16] The compounds were prepared and handled under purified Ar either in a glove box or on a vacuum line. Samples containing single crystals of $NaBa_2O$ were prepared as follows: Metallic barium (Merck, 99.0 %, distilled twice with heating at 1270 K in vacuum to remove hydrogen), BaO_2 (Merck, 93 %), and Na/K alloy (Na, Merck, 99 % and K, Merck, 98.0 %, jointly filtered through a glass filter after being melted in an Ar stream) were mixed in the approximate $Na_{15}K_7Ba_3O$ stoichiometry and sealed in a Ta ampoule under Ar. The latter was sealed in a Duran glass ampoule and treated at 620 K for ten days, followed by cooling to room temperature at 1 K h^{-1}. Needle-shaped single crystals of $NaBa_2O$ were manually selected from the resulting liquid alloy. Single-crystal diffraction studies were carried out on such crystals individually sealed in glass capillaries. Alternatively, small batches of crystals (ca. 50 mg) could be manually gathered for either powder X-ray investigations or elemental analysis. The bulk product, after removal of the liquid alloy in a press, contained about 50 wt % of $NaBa_2O$ according to powder X-ray analysis, contaminated by cubic NaBa and hexagonal Na_2Ba. Bulk $NaBa_2O$, contaminated by NaBa and BaO (ca. 50 wt % $NaBa_2O$), can also be prepared from a mixture of NaBa and Na_2O in a 2:1 molar ratio at 520 K. Single-phase samples

of $NaBa_2O$ could not be prepared; an excess of Na and Ba in the reaction mixture is necessary to stabilize the compound, and this in turn results in the contamination of the product by NaBa and Na_2Ba upon cooling. In a temperature-dependent Guinier measurement[17] pure $NaBa_2O$, obtained from ground single crystals and mixed with powdered glass to reduce absorption effects, begins to decompose to BaO at around 435 K with full decomposition at 490 K. On the other hand, when a sample containing excess Na and Ba is heated, the diffraction lines of $NaBa_2O$ can be observed up to 525 K. However, reaction of the samples with glass could not be excluded under these conditions.

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[18] Details of the crystal-structure solution and refinement based on single-crystal data: CAD-4 diffractometer, crystal size $0.2 \times 0.15 \times 0.1$ mm, orthorhombic, space group *Cmma* (no. 67), $a = 6.5907(3)$, $b = 15.327(1)$, $c = 6.9385(5)$ Å, Ba in $8m$ $(0,y,z)$ with $y = 0.08701(2)$ and $z = 0.19869(5)$, Na in $4g$ $(0,\frac{1}{4},z)$ with $z = 0.6889(7)$, O in $4a$ $(\frac{1}{4},0,0)$, $V = 700.90(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.973$ g cm^{-3}, $2\theta_{max} = 49.94°$, $Ag_{K\alpha}$ radiation, $\lambda = 0.56086$ Å, ω-θ scan, measured at 293 K, 2618 collected and 703 unique reflections ($R_{int} = 0.0216$), absorption correction: ψ-scan, $\mu = 5.877$ mm^{-1}, crystal structure solved using direct methods (SHELXS 97[19]), full-matrix least-squares refinement (anisotropic for all atoms) on F^2 (SHELXL 97[19]), 15 parameters refined, $R1(I > 2\sigma(I)) = 0.0297$, $wR2(I > 2\sigma(I)) = 0.0768$, $R1$(all data) = 0.0309, $wR2$(all data) = 0.0777, GOF = 1.183. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411905.

[19] SHELXTL Version 5.1, Bruker AXS, **1998**.

[20] Powder X-ray diffraction data, collected on samples of ground single crystals sealed in capillaries,[16] was used for full-profile Rietveld refinement; the CSD Package[21] was employed. The atomic positions obtained were consistent with those from the refinement of the single-crystal data, though less accurate. The thermal displacement parameters had to be fixed; the unit cell parameters were refined to $a = 6.5916(3)$ Å, $b = 15.3282(8)$ Å, and $c = 6.9628(4)$ Å with $R_{int} = 0.082$ and $R_{profile} = 0.252$.

[21] "CSD—Universal program package for single crystal and/or powder structure data treatment": L. G. Akselrud, Yu. N. Grin, P. Yu. Zavalij, V. K. Pecharsky, V. S. Fundamenskii, *12th European Crystallographic Meeting*, Moscow, **1989**, *3*, 155 (http://imr.chem.binghamton.edu/zavalij/CSD.html).

[22] Elemental analysis (%) of single-crystal batches: found (calcd): Ba 84.5 and 84.8 (87.6), Na 8.3 and 8.7 (7.3), O 4.1 and 4.2 (5.1), K 1.1 and 1.3 (0); these results are consistent with a small impurity of the Na/K alloy. The metal content was determined using ICP atomic emission spectrometry (TJA IRIS Advantage) after dissolving the samples in aqueous acid. Oxygen was determined as CO by measuring IR absorption after melting the samples with excess graphite (Exhalograph EAO 220, Balzers). The hydrogen content was measured by oxidizing the samples in oxygen at 1320 K and determining the amoung of released water by IR spectroscopy. Analyses of larger bulk samples containing about 50 wt% $NaBa_2O$ yielded 0.008 and 0.012 wt% H. This corresponds to no more than one hydrogen atom per 15 $NaBa_2O$ formula units.

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[30] The consideration of the crystal volume of $NaBa_2O$ also provides an additional argument against a possible contamination by hydrogen: Inclusion of hydride would rather decrease the crystal volume. Thus the value of $V(NaH) + V(BaH_2) + V(BaO) = 126.8$ Å^3, an approximation for the crystal volume of hypothetical ionic $Na^+(Ba^{2+})_2O^{2-}(H^-)_3$, is clearly too small.

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Reactions of Et_4Bi_2 with tBu_3M (M = Al, Ga)—Synthesis of Complexes with a Bidentate Dibismuthane Ligand**

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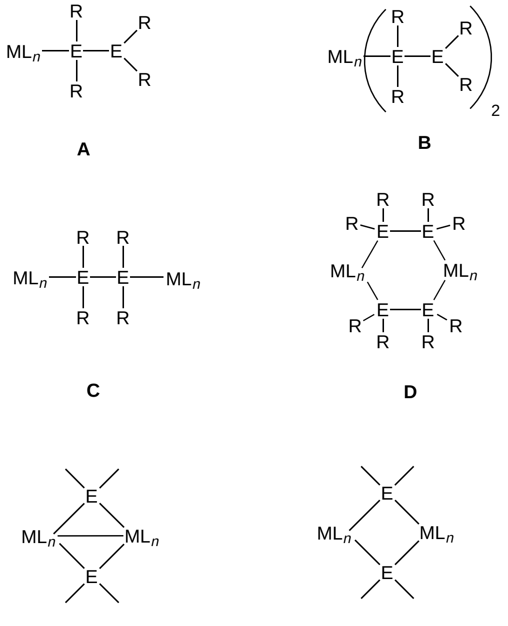
Martin Nieger

Dedicated to Professor Oskar M. Glemser
on the occasion of his 90th birthday

Since Cadet's discovery of the "fuming liquid" in 1757, numerous tetraorganodipnicogens of the type R_4E_2 (E = P, As, Sb) containing a central E–E bond have been synthesized.[1] Detailed investigations on their reactions with transition metal complexes showed their ability to form monodentate (Scheme 1, type A and B) and bidentate complexes (type C and D) under preservation of the central E–E bond. In addition, heterocycles (type E and F) were formed under E–E bond cleavage.[1, 2]



Scheme 1. Coordination modes for transition metal complexes with dipnicogen ligands R_4E_2.

In contrast, reactions with main group metal complexes such as Group 13 trialkyl compounds have been investigated to a far lesser extent. $[Me_4P_2][BH_3]_2$ (type C) was synthesized almost 50 years ago by Nöth and Burg;[3] however, the only structurally characterized compounds known were $Me_4P_2(BH_3)_2$[4] and $Me_4P_2(BH_2Br)_2$[5] prior to our recent

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