Subnitridometalates

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Chemical Twinning of Salt and Metal in the Subnitridometalates $Ba_{23}Na_{11}(MN_4)_4$ with M = V, Nb, Ta

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Abstract: *The subnitridometalates $Ba_{23}Na_{11}(MN_4)_4$ (M = V, Nb, Ta) crystallize in a new structure type, which shows ionic ortho-nitridometalate anions and motifs from simple (inter)-metallic packings: Na-centered [Na_8] cubes as cutouts of the bcc structure of elemental Na and Na-centered [$Ba_{10}Na_2$] icosahedra as found in Laves phases, for example. Single-crystal and powder X-ray diffraction studies in combination with quantum-chemical calculations of the electronic structure and Raman spectroscopy support the characterization of the subnitridometalates as "chemical twins". They consist of independent building units with locally prevalent ionic or metallic bonding in an overall metallic compound.*

In recent years, several ternary alkali-metal suboxometalates with the composition A_9MO_4 (A = Rb, Cs; M = Al, Ga, Fe, Sc, In)[1] and $Cs_{10}MO_5$ (M = Al, Ga, Fe)[2] have been described. The chemical bonding in these subvalent compounds can be described as ordered intergrowth of low-dimensional ionic structural compartments in a metallic matrix, as first established for alkali-metal suboxides.[3] The intergrowth can be seen as a special case of ordered heterostructures, namely as a chemical twin. The suboxometalates expanded the structural chemistry of the suboxides by replacing monoatomic oxide anions with complex *ortho*-oxometalate anions. Alkaline-earth subnitridometalates now expand the chemistry of binary subnitrides, for example, Ba_2N or Ba_3N,[4] to structures with complex *ortho*-nitridometalate anions. All three subnitridometalates $Ba_{23}Na_{11}(MN_4)_4$ (M = V, Nb, Ta) crystallize isotypically in the tetragonal crystal system with the space group $P4_2/n$.[7] The crystal structure contains three distinct building blocks: *ortho*-nitridometalate anions $[MN_4]^{7-}$, centered [Na@Na_8] cubes, and centered [Na@$Ba_{10}Na_2$] icosahedra (Figure 1). The tetrahedral $[MN_4]^{7-}$ anions show geometric details that are in good agreement with those of known ionic nitridometalates (Table 1). The M–N bond is only weakly influenced by the metallic surrounding in the subnitridometalates and was investigated by Raman spectroscopy on single-crystal samples of $Ba_{23}Na_{11}(VN_4)_4$, $Ba_{23}Na_{11}(NbN_4)_4$, and $Ba_{23}Na_{11}(TaN_4)_4$ (Figure 2). In each case, we observed a single broad signal with a maximum

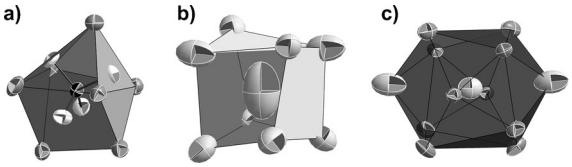
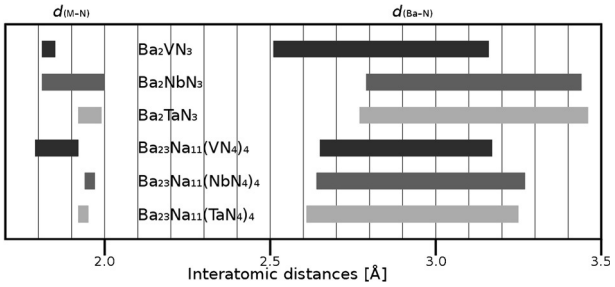


Figure 1. Coordination polyhedra in $Ba_{23}Na_{11}(MN_4)_4$. a) [Ba_7MN_4] augmented triangular prism. b) Distorted [Na_8]Na cube. c) Distorted [$Ba_{10}Na_2$]Na icosahedron. M (M = V, Nb, Ta) black, Ba dark gray, Na light gray, N white. Ellipsoids are drawn at 90% probability.

Table 1: Selected geometric details of ionic nitridometalates from the literature and the new subnitridometalates.

Compound	$d_{(M-N)}$ [Å]	$d_{(Ba-N)}$ [Å]
Ba_2VN_3[8]	1.81(4)–1.854(8)	2.51(4)–3.162(18)
Ba_2NbN_3[8]	1.876(13)–2.000(10)	2.792(12)–3.435(12)
Ba_2TaN_3[8]	1.921(13)–1.989(9)	2.772(13)–3.461(18)
$Ba_{23}Na_{11}(VN_4)_4$	1.788(16)–1.822(17)	2.652–3.174(16)
$Ba_{23}Na_{11}(NbN_4)_4$	1.940(7)–1.969(7)	2.640(7)–3.270(7)
$Ba_{23}Na_{11}(TaN_4)_4$	1.926(10)–1.950(10)	2.611(8)–3.250(10)



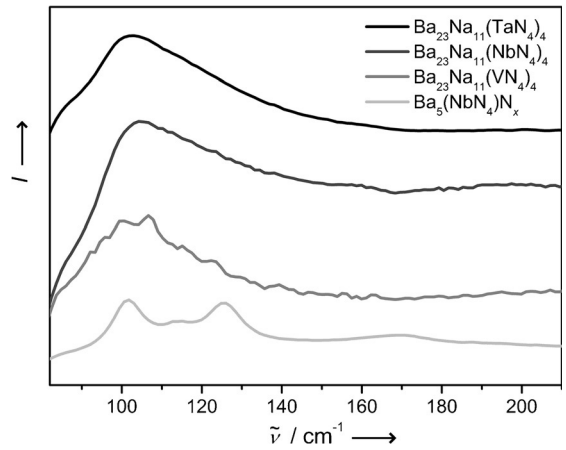


Figure 2. Raman spectra of $Ba_{23}Na_{11}(TaN_4)_4$ (black), $Ba_{23}Na_{11}(NbN_4)_4$ (dark gray), $Ba_{23}Na_{11}(VN_4)_4$ (medium gray), and $Ba_5(NbN_4)_4N_x$ (light gray).

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at low wavenumbers between 102 cm^{-1} and 106 cm^{-1}. As literature data for the Raman frequencies of $[MN_4]^{7-}$ are unavailable, a single crystal of $Ba_5(NbN_4)_4N_x$ was analyzed under similar conditions as a reference.[9] Its spectrum shows two signals at 102 cm^{-1} and 125 cm^{-1}, which correspond to two of the four Raman-active vibration modes of the tetrahedral $[NbN_4]^{7-}$ species. A regular MX_4 tetrahedron is expected to show one A_1, one E, and two F_2 vibration modes. We could assign the two signals to the A_1 (stretching vibrations only) and the E mode (deformation vibrations only). The much weaker F_2 modes could not be detected owing to high background noise. For $Ba_{23}Na_{11}(MN_4)_4$, broad signals were observed extending over a range from 85 cm^{-1} to 140 cm^{-1} with asymmetric broadening to higher wavenumbers. These signals cover the range expected for the four vibration modes of tetrahedral $[MN_4]^{7-}$ anions, and the loss of resolution with respect to the spectrum of $Ba_5(NbN_4)_4N_x$ may be attributed to the metallic behavior and the resulting optical phonons. Similar observations were made for intermetallic compounds, such as $MgCu_2$-type Laves phases.[10]

The ionic nitridometalate anions $[MN_4]^{7-}$ are coordinated by augmented triangular prisms (Johnson polyhedron J_{49})[11] of seven Ba atoms (Ba2 to Ba7; see the Supporting Information, Tables S2–S4). The four crystallographically independent N atoms are located on two triangular and two square faces of the Johnson polyhedron (Figure 1a). The augmented trigonal prisms are connected to tetramers through common edges. This results in two sets of Ba atoms, namely terminal ones (Ba2, Ba3, and Ba4) and connecting ones (Ba5, Ba6, and Ba7; the latter being centered in the tetramer of augmented trigonal prisms), correlating with two sets of slightly different anisotropic thermal displacement parameters for the Ba atoms (see Tables S5–S7). Bonding within the $[Ba_7MN_4]$ prisms is prevalently ionic, as the Ba–N distances agree with those in the respective ionic compounds Ba_2VN_3, Ba_2NbN_3, and Ba_2TaN_3 (Table 1).

These ionic blocks are twinned with a metallic substructure consisting of two distinct motifs that are best described as cutouts from well-known simple metallic structure types.

The first motif is a distorted centered $[Na@Na_8]$ cube of sodium atoms (Na2 and Na4) coordinated to the central Na1 atom (Figure 1b). This arrangement strongly resembles the bcc structure of elemental sodium. The distortion of the cube leads to two sets of Na–Na distances: Na2 is further away from the central Na1 atom (3.875(6) Å) than Na4 (3.509(8) Å). The average of 3.692 Å is only about 1% larger than the Na–Na distance in metallic Na (3.656 Å).[12] Na4 connects the sodium cube with the second metallic structural motif, resulting in the considerable distortion of the cube. Analysis of the interatomic distances (see Tables S8–S10), combined with the large anisotropic thermal displacement parameter of Na1 (Figure 1b and Tables S5–S7), corroborates the metallic character of Na1 or even suggest a $Na^{\delta-}$ atom. This situation would be comparable to the Cs atom in Cs_9MO_4, which is only in contact with other Cs atoms.[1]

The second metallic structural motif is a $[Na@Ba_{10}Na_2]$ icosahedron with Na3 at the center (Figure 1c). Na3 is coordinated by two Na1 atoms and by Ba1 to Ba5. Ba1 does not participate in the $[Ba_7MN_4]$ prisms while the $[Ba_7MN_4]$ prisms and $[Na@Ba_{10}Na_2]$ icosahedra are connected by Ba3 through common vertices and by Ba2, Ba4, and Ba5 through common edges (Figure 3). In contrast to Laves phases, for

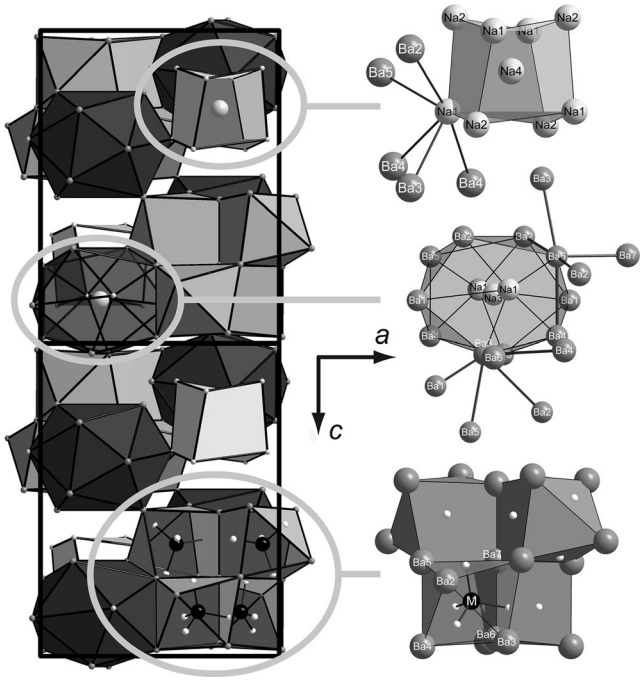

Figure 3. Crystal structure of $Ba_{23}Na_{11}(MN_4)_4$ along the crystallographic *b* axis. Augmented triangular prisms dark gray, distorted cubes light gray, distorted icosahedra black.

example, $BaNa_2$, the icosahedral coordination consists of ten Ba and two Na atoms (6 Ba and 6 Na atoms in $BaNa_2$), leading to significantly larger Na–Na distances (Na1–Na3: 4.387(9) Å in $Ba_{23}Na_{11}(NbN_4)_4$ compared to 3.72 Å in $BaNa_2$). Apparently, the higher number of Ba atoms in the $[Na@Ba_{10}Na_2]$ icosahedron prevents the formation of closer Na–Na contacts as found for the icosahedral $[Na@Ba_6Na_6]$ coordination in $BaNa_2$, and the Na–Na distances are forced to adopt values that are close to typical Ba–Na distances (see Tables S8–S11). The average Ba–Na distance in the $[Na@Ba_{10}Na_2]$ icosahedra amounts to 4.311 Å (ca. 1% larger than 4.27 Å in $BaNa_2$).[6] The icosahedral void may thus be filled with larger metal atoms, such as K, Rb, or Cs.

The crystal structure of the barium sodium subnitridometalates is built from the abovementioned structural motifs by sharing common atoms: One Na atom of the $[Na@Na_8]$ cube is also an apical atom of an $[Na@Ba_{10}Na_2]$ icosahedron, and terminal Ba atoms of the ionic $[Ba_7MN_4]$ prisms participate in the icosahedron as well. There is a clear distinction between the Ba atoms belonging only to the ionic substructure in the sense of closer distances to the neighboring atoms (suggesting Ba^{2+} cations) and those Ba atoms in the partially metallic structures with longer distances to their respective neighbors, pointing towards metallic behavior. This diversification of atoms of one and the same element owing to different bonding modes is known from alkali-metal suboxides and subnitrides of alkaline-earth metals and alkali metals.[1,3,4]

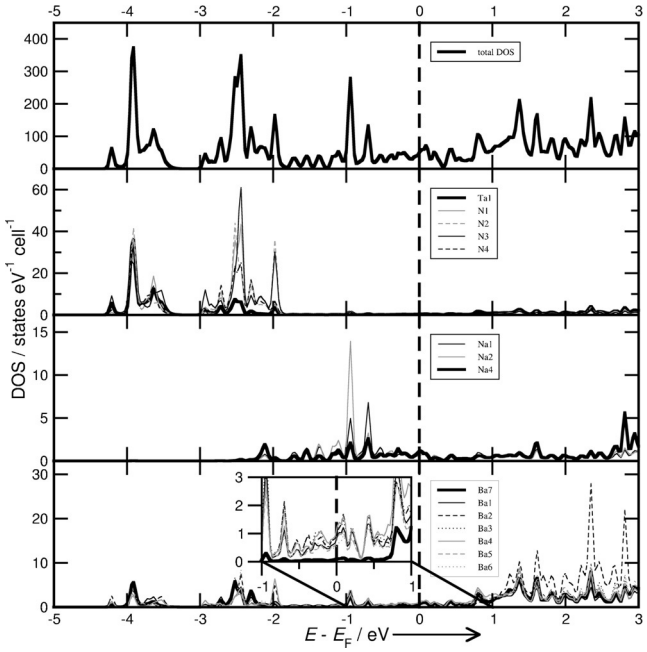

Figure 4. DOS calculated for $Ba_{23}Na_{11}(TaN_4)_4$. Top to bottom: total DOS; partial DOS for the atoms of the TaN_4 anions; partial DOS for the Na atoms of the metallic [Na@Na_8] cube; partial DOS of all Ba atoms. Inset: Magnified view of the region close to E_F.

The calculated electronic structure of $Ba_{23}Na_{11}(TaN_4)_4$ emphasizes the picture of independent building units with either metallic or ionic character, resulting in overall metallic behavior and a "chemical twin". The total density of states (DOS) and selected partial densities are shown in Figure 4. The total DOS shows no band gap at the Fermi level, hence $Ba_{23}Na_{11}(TaN_4)_4$ is a metal. The sharp bands between about −4 and −2 eV were attributed to the anionic $[TaN_4]^{7-}$ part. These bands with low dispersion resemble the band structure representation of an MO scheme for the quasi-molecular tetrahedral anion, and only few interactions with adjacent Ba atoms could be observed. The Ba atoms have different surroundings, most of them being part of metallic [Na@$Ba_{10}Na_2$] icosahedra and at the same time coordinating the nitridotantalate anions. These Ba atoms show low but significant electron density at the Fermi level and contribute to the metallic behavior. Only Ba7, the center of the tetrameric $[Ba_{19}(TaN_4)_4]$ unit (Figure 3, bottom), is different. It is not in contact with metallic parts of the structure and shows no electron density at the Fermi level, corresponding to a real Ba^{2+} cation. The Ba states show mixing with the $[TaN_4]^{7-}$ states but almost no interaction with the states of the [Na@Na_8] cubes. These cubes consist of metallic Na atoms as they all show considerable and similar electron densities at the Fermi level, supporting the presence of Na^0 atoms rather than Na^+ cations. Thus the well-segmented total DOS can be deconvoluted into the contributions of the three different building units, emphasizing the picture of chemical twinning.

In conclusion, with the barium sodium subnitridometalates of V, Nb, and Ta, we have presented a new class of subvalent compounds with tetrahedral nitridometalate anions. There is, however, no reason for subnitridometalates to be limited to these metals. Further expansions of this structure class seem promising in different ways. Transition metals with radii and valence electron concentrations similar to those of V, Nb, and Ta as well as pentavalent main-group elements such as As, Sb, Bi, or even P could be incorporated into the anionic sublattice. Various mixed crystal series from the isotypic compounds should be viable, comparable to the suboxometalates.[1,2] Modifications of the metallic sublattice should also be feasible. Akin to alkaline-earth metal subnitrides and alkali metal suboxides, the content of metallically bound alkali-metal atoms may be increased or reduced. The voids within the Ba/Na icosahedra seem large enough to incorporate metal atoms such as K, Rb, or Cs, or perhaps also alkaline-earth metals. This opens new possibilities to unite ionic and metallic aspects and properties in one material, and to change them independently as the different sublattices show only marginal interaction.

Experimental Section

The subnitridometalates were synthesized by reaction of Ba_2N (made from the elements, purity confirmed by Rietveld refinement with the software TOPAS Academic4;[13] see Figure S2), Ba (distilled, 99.95%, SMT Metalle Wimmer, Weinburg, Austria), M (M = V, Nb, or Ta; powder, 99.5%, Alfa Aesar, Karlsruhe, Germany or Merck, Darmstadt, Germany), and Na (distilled, MPI für Festkörperforschung Stuttgart, Germany) at 500 °C in argon atmosphere. Typical sample amounts were 1.5 g with a molar ratio of Ba_2N/Ba/M/Na = 8:5:2:15. Employing tantalum crucibles led to the partial occupation of the vanadium positions in $Ba_{23}Na_{11}(VN_4)_4$ with 7.0(5)% Ta, as shown by single-crystal structure refinement. The formation temperature of the subnitridometalates is low with respect to the melting temperatures of Ba (729 °C) and Ba_2N (> 900 °C, according to temperature-dependent powder diffractometry; see Figure S1). Higher temperatures led to the formation of simple ionic nitridometalates and to reaction of the starting material mixture with the crucible materials. The necessarily low reaction temperatures could be realized with the help of a Ba/Na flux. Appropriate reaction temperatures and the respective Ba/Na ratios were taken from the phase the diagram of the binary Ba–Na system.[5] As a consequence, reaction products were always accompanied by BaNa[6] as observed in the Rietveld refinements (see Figures S3–S5) according to Equation (1).

$$10\,Ba + 16\,Ba_2N + 30\,Na + 4\,M \rightarrow Ba_{23}Na_{11}(MN_4)_4 + 19\,BaNa \quad (1)$$

Syntheses leading to phase-pure products would require higher nitride contents in the starting material mixture. As a barium nitride Ba_3N_2 is unknown and sodium nitride Na_3N is not available in larger quantities, Ta_3N_5 would be the only feasible possibility to supply more nitride; however, V_3N_5 and Nb_3N_5 are unknown. The use of azides such a $Ba(N_3)_2$ or NaN_3 is rather unpromising as the evolving nitrogen would not be reactive at the low temperatures. At the moment, we are trying to establish alternative synthetic routes leading to lower amounts of or no accompanying phases; however, the difficulty consists of the necessity for low reaction temperatures for the formation of subnitridic phases while the temperature for complete reaction of the starting material mixture increases with the nitridic content.

A general problem that is encountered when Ba-rich compounds are synthesized from metallic Ba is possible hydride formation. To discern whether particular hydrides are incorporated or not is of especially high importance when compounds receive attention owing to electronically non-precise formal charge distributions. A quite obvious hint for the absence of hydridic species is the observation that in all experiments, the subnitride phases were the major components and not minor byproducts. Further evidence was obtained by solid-

state ^{1}H NMR spectroscopy (see Figure S6). Quantitative hydride incorporation in the subnitridometalates would lead to sharp and significant signals even in stationary spectra, at chemical shifts of about −6 to −8 ppm.[15] The observed broad and weak signal around 0 ppm is most probably caused by traces of hydrolysis products of the delicate samples or by traces of humidity in the NMR rotor walls.

For single-crystal structure analysis,[7] suitable specimens were isolated under dry paraffin oil, sealed in oil-filled glass capillaries, and checked for crystal quality on the respective diffractometer systems (see Table S1).

The DFT calculations of the electronic band structure were performed with the program package WIEN2000, employing the full potential linearized augmented plane wave (FP-LAPW) method. The exchange and correlation functional of Perdew, Burke, and Ernzerhof with generalized gradient approximation (GGA) was applied. The Muffin–Tin radii were set to 2.5 a_0 for Ba and Na, to 1.97 a_0 for Ta, and to 1.61 a_0 for N. The number of basis functions was determined by the value of $r_{mt}k_{max}=7$, with k_{max} as the largest k vector. The separation energy was set to −6 Ry. 18 k points in the Brillouin zone (3 thereof in the irreducible Brillouin zone) were calculated in a $3\times3\times2$ Monkhorst–Pack grid.[16]

For Raman spectroscopic analysis, a He–Ne laser with a 1 mm focus in a confocal Raman microscope (LabRSM HG UV/Vis, Horiba Jobin Ivon GmbH, München, combined with an Olympus BX 41 microscope) equipped with a CCD detector was focused on $Ba_{23}Na_{11}(MN_4)_4$ single crystals in capillaries filled with dry paraffin oil. For comparison, a $Ba_5(NbN_4)_4N_x$ single crystal was measured under identical conditions.

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Keywords: band structure calculations · polar metals · Raman spectroscopy · structure elucidation · subnitridometalates

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[7] a) $Ba_{23}Na_{11}(VN_4)_4$: $T=293$ K; tetragonal, space group $P4_2/n$ (No. 86), $a=14.131(17)$ Å, $c=18.537(2)$ Å, $V=3703.0(9)$ Å^3, $Z=2$, $\rho=3.476$ g cm^{-3}; diffractometer: Bruker D8-Quest ($Mo_{K\alpha}$ radiation, Göbel mirror); $2\theta_{max}=50.00°$; 29461 observed intensities, 3217 unique; Lorentz, polarization, and semi-empirical absorption correction;[14] least-squares refinement on I (all atoms anisotropic) with SHELXL97;[14] 125 free variables, R values ($I\geq2\sigma(I)$): $R1=0.0823$, $wR2=0.1259$; min/max residual electron density: −2.461/+2.303 e$^-$ Å^{-3}; b) $Ba_{23}Na_{11}(NbN_4)_4$: $T=293$ K; tetragonal, space group $P4_2/n$ (No. 86), $a=14.3724(9)$ Å, $c=18.8431(47)$ Å, $V=3892.3(4)$ Å^3, $Z=2$, $\rho=3.419$ g cm^{-3}; diffractometer: STOE IPDS-1 ($Mo_{K\alpha}$ radiation, graphite monochromator); $\mu(Mo_{K\alpha})=12.047$ mm^{-1}; $2\theta_{max}=55.00°$; 39074 observed intensities, 4479 unique; Lorentz, polarization, and numerical absorption correction;[14] least-squares refinement on I (all atoms anisotropic) with SHELXL97;[14] 123 free variables, R values ($I\geq2\sigma(I)$): $R1=0.0373$, $wR2=0.0653$; min/max residual electron density: −1.359/+1.375 e− Å^{-3}; c) $Ba_{23}Na_{11}(TaN_4)_4$: $T=293$ K; tetragonal, space group $P4_2/n$ (No. 86), $a=14.3603(12)$ Å, $c=18.7552(17)$ Å, $V=3867.7(6)$ Å^3, $Z=2$, $\rho=3.744$ g cm^{-3}; diffractometer: STOE IPDS-1 ($Mo_{K\alpha}$ radiation, graphite monochromator); $\mu(Mo_{K\alpha})=17.186$ mm^{-1}; $2\theta_{max}=55.00°$; 38628 observed intensities, 4447 unique; Lorentz, polarization, and semi-empirical absorption correction;[14] least-squares refinement on I (all atoms anisotropic) with SHELXL97;[14] 123 free variables, R values ($I\geq2\sigma(I)$): $R1=0.0387$, $wR2=0.0590$; min/max residual electron density: −1.007/+1.719 e$^-$ Å^{-3}; d) further details on the crystal-structure investigations 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 numbers CSD-431345 ($Ba_{23}Na_{11}(VN_4)_4$), CSD-431343 ($Ba_{23}Na_{11}(NbN_4)_4$), and CSD-431344 ($Ba_{23}Na_{11}(TaN_4)_4$).

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