Directed Syntheses of New Quaternary Niobium Oxysulfides: Crystal Structures and Properties of $K_4Nb_2S_{10}O$ and $Rb_4Nb_2S_{10}O$ Compared to $K_4Nb_2S_{11}$

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The new compounds $K_4Nb_2S_{10}O$ and $Rb_4Nb_2S_{10}O$ have been synthesized by the reaction of potassium or rubidium alkaline polychalcogenides with NbO_2, Nb_2O_5, or mixtures of Nb and NbO. Their structures consist of discrete $[Nb_2Q_{11}]^{4-}$ anions (Q = O, S) built up of two face-sharing pentagonal bipyramids, which are connected via the alkali metal cations.

Introduction

Difficulties are encountered in syntheses of oxysulfides and oxyselenides of the Group 5 transition metals owing to the high oxophilicity of these metals. If there is a competition between the hard O^{2-} anion and the more polarizable chalcogenide anions Q^{2-} (Q = S, Se, Te), Group 5 metals (M = V, Nb, Ta) prefer to bond to oxygen. Previously reported compounds containing both oxygen and another chalcogen bound to the metal atom were obtained serendipitously because oxygen-contaminated starting materials were used in the attempted synthesis of other compounds. Traces of such oxygen-containing compounds are sufficient to partially substitute heavier chalcogenide anions, hence oxysulfides or oxometallates are obtained as side products. However, such compounds are of special interest because they combine the physical properties of pure transition metal chalcogenides with those of the pure oxides. Therefore, the directed synthesis of oxysulfides and oxyselenides is a challenge for the preparative solid-state chemist.

In the field of classical solvent-based chemistry, several compounds containing thiooxometallate units have been synthesized. It is assumed that an important step in the addition of oxygen is the hydrolysis of sulfidic species. Examples of such compounds reported previously are $R_2[Nb(O)(S_2)_2SH]$ and $R_4\{[Nb(S)_3]_2O\}$ (with R = Ph_4P^+, Et_4N^+),[1a] $R_2\{[(S_2)_2MoO]_2S\}$ and $R_2\{[(S_2)_2MoO]_2S]S\}_2$ (with R = Et_4N^+).[1b] The vanadium compound $(NH_4)_6(V_4S_{20}O_4) \cdot 5\ bpy \cdot 7\ H_2O$[2] is also known. It must also be noted that numerous ternary alkali oxysulfides of the composition $[MO_{4-x}S_x]^{2-}$ (M = Mo, W, Re) have been precipitated from aqueous solutions.[3a−3f]

In contrast to the numerous solvent-mediated reactions, examples of alkali or alkaline earth transition metal oxysulfides and -selenides prepared by solid-state reactions are rare. Examples are $Ba_6(NbS_4)(NbS_3O)_3$,[4] $Na_{1.9}Cu_2Se_2\cdot Cu_2O$,[5] $Ba_6Ti_5S_{15}O$,[6] $Na_{1.9}Cu_2Se_2\cdot Cu_2O$,[5] $A_4(UO_2)(S_2)$ (A = Na, Cs),[7] and $Na_4(UO_2)Cu_2S_4$.[8] $Ba_6(NbS_4)(NbS_3O)_3$ was obtained as a by-product during a classical high-temperature synthesis at 1273 K, the oxygen source being identified as $BaSO_4$.[4] The other compounds were prepared using the reactive flux method.

In the course of our investigations of A−M(V)−Q systems (A = alkali metal; M = V, Nb, Ta; Q = S, Se, Te), we have prepared several new compounds containing M_2Q_{11} units as basic building blocks.[9,10a] In this unit, the Nb atoms are sevenfold coordinated by chalcogen atoms and the polyhedron may be described as a distorted pentagonal bipyramid.

This unit can be connected in many different modes. In $K_4Nb_2S_{11}$[9,10a] and $Rb_4Ta_2S_{11}$,[9,10b] isolated monomeric species are found, whereas in $K_4Nb_2S_{14}$[10c] this unit is expanded by an additional polychalcogenide ligand. In $A_6Nb_4S_{22}$ (A = Rb, Cs),[10d] two of these units are directly connected, while in $K_6Nb_4S_{25}$ they are joined via one additional S_3 fragment.[10e] For the selenides, predominantly polymeric structures are found. $K_{12}Nb_6Se_{35}$ and $Rb_{12}Nb_6Se_{35}$[10f] are built up from infinite ${}_\infty^1[Nb_6Se_{35}]^{12-}$ anionic chains, in which the Nb_2Q_{11} units are linked either directly or through one Se atom. It must be pointed out that all geometrical changes on going from monomeric to dimeric or polymeric species can be rationalized on the basis of a simple topological description.[9] In the course of our efforts to synthesize further polymeric compounds, we have obtained two new compounds, which surprisingly contain oxygen in one of the terminal positions of the bipyramid. In $K_4Nb_2Se_{11}O$,[10g] infinite anionic chains are found, in which the M_2Q_{11} units are connected through one Se atom. In contrast, crystals of $Cs_4Nb_2Se_{11}O$[10g] contain both discrete monomeric anions and polymeric anions, where the latter are built up of Nb_2Q_{11} units connected either directly or through one additional Se_2 unit.

A careful analysis of the experimental conditions showed that the source of oxygen was a contamination of the niobium metal with niobium oxides. However, the accidental synthesis of the new niobium oxyselenides prompted us to

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try to prepare oxysulfides and -selenides in a directed way. For the first investigations we selected the simplest compounds containing discrete monomeric Nb_2Q_{11} units. Here, we report on the directed syntheses of the two new oxysulfides $K_4Nb_2S_{10}O$ and $Rb_4Nb_2S_{10}O$. The structural and optical properties of these two new compounds are compared with those of the previously reported oxygen-free potassium compound.[10a]

Table 1. Selected bond lengths [Å], deviation of the Nb atoms from the pentagonal plane [Å], and angles between the pentagonal planes [°] for $Rb_4Nb_2S_{10}O$, $K_4Nb_2S_{10}O$, and $K_4Nb_2S_{11}$

Bond lengths	$Rb_4Nb_2S_{10}O$	$K_4Nb_2S_{10}O$	$K_4Nb_2S_{11}$[10a]
Nb(1)−S(1)	2.225(3)	2.229(3)	2.221(3)
Nb(1)−S(2)	2.440(2)	2.435(3)	2.457(3)
Nb(1)−S(3)	2.500(3)	2.503(3)	2.497(3)
Nb(1)−S(4)	2.504(2)	2.505(3)	2.502(2)
Nb(1)−S(5)	2.496(3)	2.487(3)	2.512(3)
Nb(1)−S(6)	2.456(3)	2.452(3)	2.436(3)
Nb(1)−S(10)	2.870(2)	2.866(3)	2.856(3)
Nb(2)−O	1.765(7)	1.796(7)	−
Nb(2)−S(11)	−	−	2.182(3)
Nb(2)−S(3)	2.935(2)	2.899(3)	2.859(3)
Nb(2)−S(4)	2.504(2)	2.498(3)	2.504(2)
Nb(2)−S(7)	2.460(3)	2.463(3)	2.464(2)
Nb(2)−S(8)	2.494(3)	2.488(3)	2.463(3)
Nb(2)−S(9)	2.484(3)	2.493(3)	2.491(3)
Nb(2)−S(10)	2.494(2)	2.481(3)	2.486(3)
S(2)−S(3)	2.071(4)	2.071(4)	2.061(3)
S(5)−S(6)	2.077(4)	2.071(5)	2.060(4)
S(7)−S(10)	2.074(4)	2.073(4)	2.070(3)
S(8)−S(9)	2.076(4)	2.073(4)	2.078(4)
Deviation of Nb from the pentagonal plane	Nb(1) 0.474 Nb(2) 0.470	Nb(1) 0.475 Nb(2) 0.473	Nb(1) 0.479 Nb(2) 0.474
Angle between pentagonal planes	128.4°	128.3°	129.4°

Results and Discussion

Crystal Structures

$K_4Nb_2S_{10}O$ and $Rb_4Nb_2S_{10}O$ are isotypic with the potassium polysulfide $K_4Nb_2S_{11}$[10a] and crystallize in the noncentrosymmetric space group *Pca*2_1. Their structures consist of well-separated $[Nb_2S_{10}O]^{4-}$ anions connected through the alkali metal ions. In the complex anion $[Nb_2S_{10}O]^{4-}$, one of the two Nb atoms is bound to a terminal monosulfide S^{2-}, while the other is coordinated by the terminal O^{2-} ligand (Figure 1, A and B). The environment about the Nb atoms is completed by one η^2-S_2^{2-} unit, one μ^2-S^{2-} unit that bridges the two Nb atoms, and one additional S_2^{2-} anion, which is bound in an η^2 fashion to one Nb while one S atom of this unit serves as a second bridging atom to the opposite Nb. Hence, the coordination mode of the anion may be described as $[Nb_2(\mu\text{-}S)(\mu\text{-}\eta^2,\eta^1\text{-}S_2)_2(\eta^2S_2)_2(S)(O)]^{4-}$ (Figure 1, A and B). The resulting coordination polyhedron can be described as being composed of two distorted pentagonal bipyramids sharing common faces. The Nb−Nb bond length of 3.538 Å in the rubidium compound and 3.522 Å in the potassium compound are significantly longer than that in metallic Nb (2.858 Å), too long for an Nb−Nb bond (Table 1). Hence, the formal oxidation state of Nb can be assigned as +5.

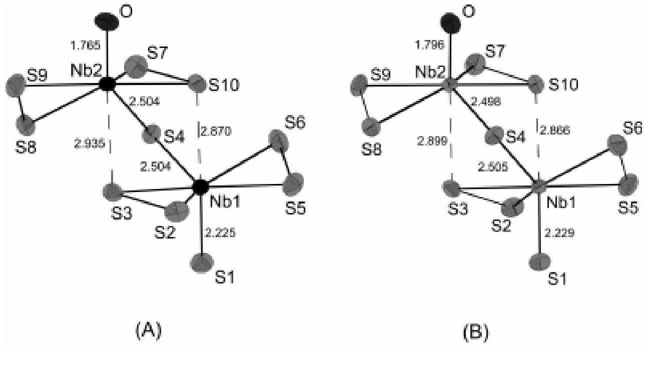

Figure 1. Structure of the $[Nb_2S_{10}O]^{4-}$ anion in (A) $Rb_4Nb_2S_{10}O$ and (B) $K_4Nb_2S_{10}O$ showing atom labelling (bond lengths are given in Å; displacement ellipsoids are drawn at a 50% probability level)

All interatomic distances in the anions of the two compounds are comparable (Table 1). The interatomic Nb−S distances may be divided into three groups. One short [Rb compound: Nb(1)−S(1): 2.225(3) Å; K compound: 2.229(3) Å], five more typical distances [Rb: Nb(1): 2.440(2) to 2.504(2) Å, Nb(2): 2.484(2) to 2.504(2) Å; K: Nb(1): 2.435(3) to 2.505(3) Å, Nb(2): 2.463(3) to 2.498(3) Å], and one longer separation [Rb: Nb(1)−S(10): 2.870(2), Nb(2)−S(3): 2.935(2) Å; K: 2.866(3), 2.899(3) Å] (Table 1). As was demonstrated in a previous communication, the long Nb−S separation must be treated as a weak interaction, while the short Nb−S bond lengths are close to an Nb−S double-bond length.[9] The S−S distances in the S_2^{2-} units range from 2.071(4) to 2.077(4) Å and are thus typical for S−S single bonds (Table 1). The Nb atoms are shifted from the plane of the pentagonal bipyramid towards the terminal chalcogen atoms by about 0.474 Å [Nb(1)] and 0.470 Å [Nb(2)] in the rubidium compound, and by 0.475 Å [Nb(1)] and 0.473 Å [Nb(2)] in the potassium compound (Table 1).

The Nb−O bond length of 1.765(7) Å [1.796(7) Å in $K_4Nb_2S_{10}O$] can be regarded as corresponding to an Nb=O double bond, and is comparable to those reported for $R_4\{[Nb(O)(Se_2)_2]_2Se_4\}$ (Nb−O: 1.671 Å) and $R_4\{[Nb(Se)_3]_2O\}$ (R = Ph_4P^+, Et_4N^+)[1a] (Nb−O: 1.682 Å), where Nb is sevenfold coordinated. In the binary oxides NbO and NbO_2, with Nb in a quadratic-planar environment, the Nb−O bond lengths are about 2.105 Å and 2.046 Å, respectively. The average Nb−O distance in a tetrahedral environment, as found in Nb_2O_5, is 1.725 Å.[11a] We note that Nb−O distances are scattered over a wide range, even those in NbO_6 octahedra (e.g. 1.751 to 2.554 Å in $Nb_{12}O_{29}$;[11b] 1.635 to 2.331 Å in $NaNbO_3$;[11c] 1.867 to 2.107 Å in $Rb_4Nb_{11}O_{30}$[11d]) and an NbO_7 pentagonal bipyramid (1.896 to 2.435 Å and 1.761 to 2.161 Å in $LaNb_5O_{14}$[11e]).

The packing of anions and cations in the rubidium compound is depicted in Figure 2, A and B. A projection onto the *a*−*b* plane reveals an almost hexagonal arrangement of the anions, with channels running parallel to the *c* axis, whereas a view parallel to [0 1 0] shows the separation of the anions by the alkali metal cations. The shortest intermolecular nonbonding S−S distances are 3.239 Å in $Rb_4Nb_2S_{10}O$ and 3.252 Å in $K_4Nb_2S_{10}O$, both of which are significantly shorter than the sum of the van der Waals radii of sulfur. The alkali metal cations are coordinated by S and O atoms in irregular polyhedra and have coordination numbers between 8 and 10. The A···S and A···O distances lie in the expected ranges for K^+ and Rb^+ cations and S^{2-} and O^{2-} anions[10d,12a,12b] (Table 2).

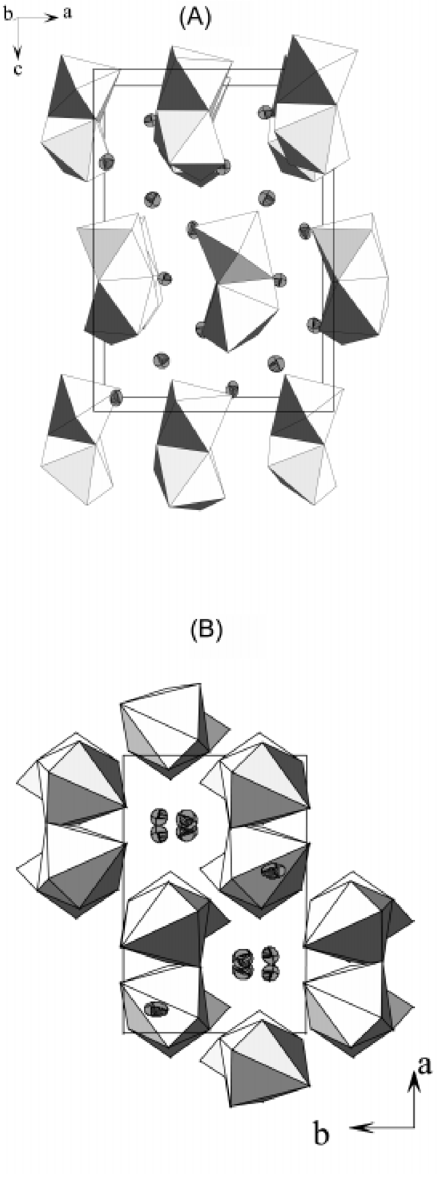

Figure 2. Crystal structure of $A_4Nb_2S_{10}O$ (A = K, Rb) showing (A) a view parallel to [0 1 0], and (B) a view parallel to [0 0 1]

Comparison of the interatomic distances in the $[Nb_2S_{10}O]^{4-}$ anion of $K_4Nb_2S_{10}O$ with those in the $[Nb_2S_{11}]^{4-}$ anion of $K_4Nb_2S_{11}$ shows that the introduction of the oxygen atom only slightly influences the distinct Nb−S distances (Table 1) The most marked deviation is observed for the Nb(2)−S(3) distance, positioned *trans* to Nb(2)−O, which is 0.040 Å longer than in $K_4Nb_2S_{11}$. The angle between the two pentagonal planes amounts to 128.3° in $K_4Nb_2S_{10}O$ and 129.4° in $K_4Nb_2S_{11}$ (Table 1).

Table 2. Coordination numbers (CN), shortest (min.), longest (max.), and average (< >) A···S distances, as well as A···O distances [Å] for the alkali metal cations (A) in $K_4Nb_2S_{10}O$, $Rb_4Nb_2S_{10}O$, and $K_4Nb_2S_{11}$ (cut-off$_K$ = 3.81 Å; cut-off$_{Rb}$ = 4.01 Å)

$Rb_4Nb_2S_{10}O$	Rb(1)	Rb(2)	Rb(3)	Rb(4)
CN	10	9	9	8
Rb···S min.	3.330(3)	3.333(3)	3.208(3)	3.347(3)
Rb···S max.	3.658(3)	3.704(3)	3.751(3)	3.804(3)
< Rb···S >	3.517(3)	3.466(3)	3.478(3)	3.532(3)
Rb···O	3.321(8)	2.993(6)	−	2.793(7)
$K_4Nb_2S_{10}O$	K(1)	K(2)	K(3)	K(4)
CN	10	9	9	8
K···S min.	3.210(4)	3.228(4)	3.103(4)	3.239(4)
K···S max.	3.614(4)	3.591(4)	3.753(4)	3.807(4)
< K···S >	3.427(4)	3.382(4)	3.387(4)	3.422(4)
K···O	3.258(8)	2.913(7)	−	2.605(8

Synthetic Aspects

As pointed out in the Experimental Section, direct syntheses of the title compounds can be carried out using several Nb oxides such as NbO, NbO_2, or Nb_2O_5, as well as mixtures of elemental Nb with these oxides. However, if only small amounts of niobium oxides are present, e.g. only slightly contaminated Nb metal is used for the syntheses, mixtures of oxysulfides and the pure sulfides are obtained. This is exemplified by the synthesis of the two new compounds, $K_4Nb_2S_{10.7}O_{0.3}$ and $Rb_4Nb_2S_{10.7}O_{0.3}$, which were isolated in the course of our investigations. Because these compounds are isotypic with the title compounds, having only very small differences in their cell parameters, their identification by means of X-ray powder diffraction is not possible. Significant differences are only observed upon refinement of single-crystal data, and only with an oxygen content of several%. For an effective control of the syntheses of pure chalcogenides, oxysulfides, or oxyselenides, this is not an adequate method. Therefore, a much more sensitive method is needed for the fast and non-destructive characterization of these compounds. For this purpose, extremely sensitive spectroscopic methods are ideal. If small amounts of oxysulfides or oxyselenides are present, this can clearly be detected by the appearance of Nb−O absorption peaks in the IR spectra. The vibration of the Nb−O bond in $Rb_4Nb_2S_{10}O$ gives rise to a strong absorption near 850 cm^{-1} (see Figure 3, B and C), whereas for the pure sulfide this band is absent (Figure 3, A). Therefore, IR spectroscopy is a suitable tool for monitoring the synthesis of compounds of this class.

It should be noted that in the title compounds only one of the two terminal positions is occupied by oxygen. Therefore, several attempts were made to substitute both axial S atoms by O atoms. A large number of experiments were carried out using different combinations of Nb with Nb oxides (NbO, NbO_2, and Nb_2O_5) as well as only Nb oxides

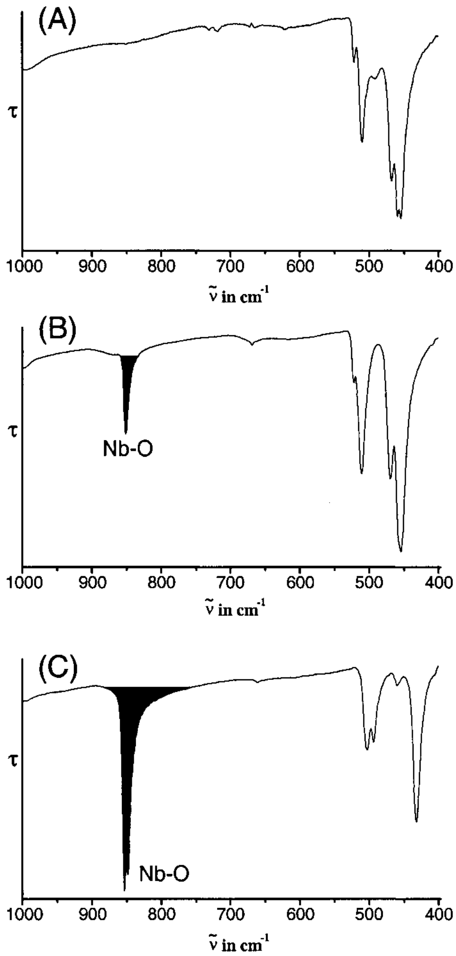

Figure 3. MIR spectra of (A) $K_4Nb_2S_{11}$, (B) $K_4Nb_2S_{10.7}O_{0.3}$, and (C) $K_4Nb_2S_{10}O$ (τ in arbitrary units)

as starting materials. However, the products of all these reactions consisted only of $Rb_4Nb_2S_{10}O$ or $K_4Nb_2S_{10}O$, alkali metal oxoniobates, and A_3NbS_4[13] (A = K, Rb) as the minor phases. In the case of the pure oxides, this is an interesting reaction from several points of view. First of all, most of the oxygen atoms of the niobium oxide must be replaced by sulfur atoms, which would be expected to be difficult considering the highly oxophilic character of Nb. Secondly, it is not obvious why only one oxygen remains unchanged, while in the products of the solution-mediated reactions both terminal positions are invariably occupied by oxygen. Concerning the reaction mechanism in the case of pure Nb_2O_5, a redox reaction between low-valent Nb and the S_x^{2-} polyanions in the melt can be excluded. Instead, it involves replacement of most of the oxygen by sulfur, where the large excess of sulfur does not allow the retention of oxygen at both the axial positions. However, even at lower concentrations, only one of the two possible positions is occupied by O. A further decrease of the sulfur content is not possible because no flux is generated. The reasons for this surprising reaction remain unclear, hence further investigations are needed.

UV/Vis Measurements

For a comparison of the optical properties, UV/Vis reflectance spectra of $K_4Nb_2S_{10}O$ and the pure sulfide were measured (Figure 4). Both compounds show a sharp absorption, from which an optical-band gap of 1.99 eV can be estimated for $K_4Nb_2S_{10}O$, while in the case of $K_4Nb_2S_{11}$ this band gap is shifted to higher energy by about 0.1 eV. The colour of the new material, as well as the value for the band gap, are consistent with its semiconducting nature.

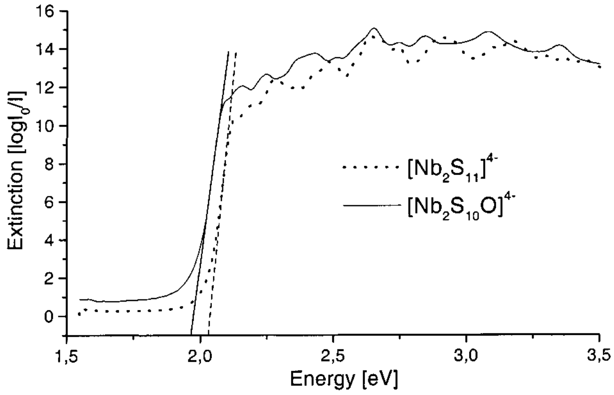

Figure 4. UV/Vis spectra of $K_4Nb_2S_{10}O$ and $K_4Nb_2S_{11}$

Conclusion

In the present paper we have shown that oxysulfides of niobium can be synthesized in a directed way by employing niobium oxides as starting materials. This synthetic approach can also be applied to selenide chemistry and we have shown that the polymeric oxyselenides first obtained accidentally can also be prepared using NbO, NbO_2, or Nb_2O_5. It can be assumed that the directed introduction of oxygen is generally applicable. However, in contrast to what is known from solution chemistry, in the reaction in the alkali metal polychalcogenide melts only one of the two terminal positions is selectively occupied by oxygen. Such reactions are not only of considerable interest from a synthetic point of view, but also to dramatically increase the number of new compounds in several ternary and multinary transition metal polychalcogenide systems. Moreover, the directed introduction offers the possibility of influencing or even modelling the physical properties of the compounds at a molecular level.

Experimental Section

Syntheses: The requisite alkali metal sulfides were first prepared by reactions of stoichiometric amounts of the elements in liquid ammonia. $K_4Nb_2S_{10}O$ and $Rb_4Nb_2S_{10}O$ were then synthesized by reactions of K_2S_3 and Rb_2S_3 with S and NbO in molar ratios of 2:4:1. As mentioned above, the preparation could also be carried out using several mixtures of Nb/NbO and NbO_2 or Nb_2O_5. The starting reagents were thoroughly mixed in a nitrogen-filled glovebox and then transferred to a Pyrex ampoule. The ampoule was evacuated to $6 \cdot 10^{-5}$ mbar and flame-sealed. The sample was heated to 623 K and maintained at this temperature for 5 d. It was then cooled to 473 K at a rate of 3 K/h and to room temperature at a rate of 30 K/h. The excess polysulfide flux was removed by washing with dry DMF and diethyl ether and the residue was dried in vacuo. After optimization of the reaction parameters, yields of 50% based on niobium were achieved. The homogeneity of the product was checked by means of X-ray powder diffraction and MIR spectroscopy.

General Remarks: Single-crystal X-ray investigations were performed with a STOE AED II diffractometer (Mo-K_α radiation, graphite monochromator). The intensities were reduced to F_o. Lorentz, polarization, and empirical absorption corrections using ψ-scan data were applied. Both structures were solved by direct methods using SHELXS-86. Full-matrix least-squares refinements were performed against F^2 using SHELXL-93. All atoms were refined using anisotropic displacement parameters. Additional material relating to the structure determination can be ordered from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the numbers. CSD-410820 and -410821, the names of the authors, and the full journal citation. − MIR spectra were recorded with a Genesis FT-IR spectrometer (ATI Mattson) in the range 400−4000 cm^{-1} with a resolution of 2 cm^{-1}. Samples of the compounds were prepared as KBr pellets. − UV/Vis diffuse-reflectance measurements were made with a Leica Orthoplan microscope equipped with a Leica MPV-SP, an ICS quartz UV optic, and a xenon lamp as light source. The resolution was 1 nm and $BaSO_4$ was used as a standard for 100% reflectance. Absorption data were calculated from the reflectance data using the Kubelka−Munk function. The approximate band gap was determined from the intersection point on the energy axis of the line extrapolated from the linear part of the absorption edge in an $[F(R)]^2$ plot. − Powder diffraction measurements were made using a STADI P transmission powder diffractometer from STOE & CIE.

X-ray Crystallographic Study. − $K_4Nb_2S_{10}O$: Mol. mass 678.82, red crystal, size: 0.3 × 0.2 × 0.2 mm, a = 12.714(3) Å, b = 7.532(2) Å, c = 17.828(3) Å, V = 1707.2(7) Å^3 (room temp.), $\rho_{calc.}$ = 2.641 g cm^{-3}, orthorhombic, $Pca2_1$ (No. 29), Z = 4, μ = 3.517 mm^{-1}, 2824 reflections measured in the range $3° < 2\theta < 53°$, 2307 independent reflections used for refinement, R_{int} = 0.0466, 154 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0417 \times P)^2 + (1.06 \times P)]$, R for 1765 $F_o > 4\sigma(F_o)$ = 0.0350, $wR2$ for all 2307 data = 0.0829, GooF = 1.028, residual electron density 1.23/−0.80 eÅ^{-3}. The absolute structure was determined and is in agreement with the selected setting: Flack x parameter = 0.03(12). − **$Rb_4Nb_2S_{10}O$:** Mol. mass 864.3, red crystal, size: 0.3 × 0.2 × 0.2 mm, a = 12.967(1) Å, b = 7.790(1) Å, c = 18.085(2) Å, V = 1826.7 Å^3 (room temp.), $\rho_{calc.}$ = 3.143 g cm^{-3}, orthorhombic, $Pca2_1$ (No. 29), Z = 4, μ = 12.97 mm^{-1}, 3843 reflections measured in the range $3° < 2\theta < 54°$, 3040 independent reflections used for refinement, R_{int} = 0.0320, 155 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0361 \times P)^2 + (0.0 \times P)]$, R for 2439 $F_o > 4\sigma(F_o)$ = 0.0316, $wR2$ for all 3040 data = 0.0714, GooF = 1.013, residual electron density 0.90/−0.79 eÅ^{-3}. The absolute structure was determined and is in agreement with the selected setting: Flack x parameter = 0.018(9).

Acknowledgments

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[1] [1b] B. S. Mandimutsira, S.-J. Chen, K. D. Demadis, D. Coucouvanis, *Inorg. Chem.* **1995**, *34*, 2267−2268. − [1b] D. Coucouvanis, A. Hadjikyriacou, *Inorg. Chem.* **1987**, *26*, 1−2.

[2] C. Simonnet-Jégat, S. Delalande, S. Halut, B. Marg, F. Sécheresse, *J. Chem. Soc., Chem. Commun.* **1996**, 423−424.

[3] [3a] A. Müller, B. Krebs, W. Rittner, M. Stockburger, *Ber. Bunsenges.* **1967**, 182−189. − [3b] A. C. Ranade, A. Müller, E. Diemann, *Z. Anorg. Allg. Chem.* **1970**, *373*, 258−264. − [3c] A. Müller, W. Rittner, A. Neumann, R. C. Sharma, *Z. Anorg. Allg. Chem.* **1981**, *472*, 69−74. − [3d] M. Herbold, G. X. Jin, A. Müller, M. Penk, *Z. Naturforsch.* **1991**, *46b*, 25−34. − [3e] A. Müller, W. Jaegermann, W. Hellmann, *J. Mol. Struct.* **1983**, *100*, 559−570. − [3f] A. Müller, O. Glemser, E. Diemann, H. Hofmeister, *Z. Anorg. Allg. Chem.* **1969**, *371*, 74−80.

[4] L. E. Rendon-Diazmiron, C. F. Campana, H. Steinfink, *J. Solid State Chem.* **1983**, *47*, 322−327.

[5] Y. P. Park, D.C. DeGroot, J. Schindler, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1993**, *5*, 8−10.

[6] A. C. Sutorik, M. G. Kanatzidis, *Chem. Mater.* **1994**, *6*, 1700−1704.

[7] A. C. Sutorik, M. G. Kanatzidis, *Polyhedron* **1997**, *16*, 3921−3927.

[8] A. C. Sutorik, M. G. Kanatzidis, *J. Am. Chem. Soc.* **1997**, *119*, 7901−7902.

[9] W. Bensch, P. Dürichen, C. Näther, *Eur. J. Solid State Inorg. Chem.*, in press.

[10] [10a] W. Bensch, P. Dürichen, *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 527−536. − [10b] P. Dürichen, W. Bensch, *Acta Crystallogr.* **1998**, *C54*, 706. − [10c] W. Bensch, P. Dürichen, *Inorg. Chim. Acta* **1997**, *261*, 103. − [10d] W. Bensch, P. Dürichen, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1963−1967. − [10e] W. Bensch, P. Dürichen, *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 1233. − [10f] P. Dürichen, M. Bolte, W. Bensch, *J. Solid State Chem.* **1998**, *140*, 97−102. − [10g] P. Dürichen, O. Krause, W. Bensch, *Chem. Mater.* **1998**, *10*, 2127−2134.

[11] [11a] B. M. Gatehouse, A. D. Wadsley, *Acta Crystallogr.* **1964**, *17*, 1545. − [11b] R. Norin, *Acta Chem. Scand.* **1966**, *20*, 871−880. − [11c] R. von der Muehl, A. Sadel, P. Hagenmüller, *J. Solid State Chem.* **1984**, *51*, 176−182. − [11d] J. C. Dewan, A. J. Edwards, G. R. Jones, *J. Chem. Soc., Dalton Trans.* **1978**, 968−972. − [11e] R. Hofmann, R. Gruehn, *Z. Anorg. Allg. Chem.* **1990**, *590*, 81−92.

[12] [12a] P. Boettcher, *Z. Kristallogr.* **1979**, *150*, 65−73. − [12b] M. Serafin, R. Hoppe, *J. Less-Common Met.* **1980**, *76*, 299−316.

[13] O. Krause, C. Näther, I. Jeß, W. Bensch, *Acta Crystallogr.* **1998**, *C54*, 902−904.

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