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# Oxygen out, sulfur in: The alkali metal sulfidotungstates $K_2[WS_4]$ and novel $Na_2[WS_4] \cdot 4H_2O$

Benjamin Knies<sup>[a]</sup> and Ingo Hartenbach<sup>\*[a]</sup>Dedicated to Professor Thomas Schleid on the occasion of his 65<sup>th</sup> birthday.

An attempt to synthesize a holmium sulfidotungstate using potassium polysulfides as reactive flux resulted in orange single crystals of  $K_2[WS_4]$ , isotypic to  $K_2[MoS_4]$  (orthorhombic; *Pnma*;  $a = 935.10(3)$ ,  $b = 694.22(2)$ ,  $c = 1221.85(4)$  pm;  $Z = 4$ ). A similar attempt to obtain a neodymium sulfidotungstate with sodium polysulfide yielded a violet substance, which underwent hydrolysis yielding orange-yellow single crystals of  $Na_2[WS_4] \cdot 4H_2O$  (monoclinic, *C2/c*,  $a = 1098.08(4)$ ,  $b = 904.46(3)$ ,  $c = 1144.27(4)$  pm,  $\beta = 101.577(3)^\circ$ ,  $Z = 4$ ). Further attempts to synthesize these products deliberately as single phase materials

only proved to be successful for  $K_2[WS_4]$  but not for  $Na_2[WS_4] \cdot 4H_2O$ . Both compounds contain non-condensed  $[WS_4]^{2-}$  tetrahedra, which surround the alkali metal cations with coordination numbers of nine and eight in  $K_2[WS_4]$ . In  $Na_2[WS_4] \cdot 4H_2O$ , the sodium cations are coordinated by two sulfide anions plus four water molecules, resulting in a coordination number of six. Besides crystal structure determination, infrared and single crystal Raman spectra were collected and the optical band gap of  $K_2[WS_4]$  was determined.

## Introduction

Compounds, consisting of tungsten and sulfur (as well as molybdenum and sulfur) are known since the days of Berzelius (about 200 years ago) and longer, since *tungstenite*, a rare mineral with the composition  $WS_2$  is found in nature.<sup>[1]</sup> Regarding sulfidotungstates(VI), there are a few compounds known to literature, which are rather well investigated, however, only with monovalent counteranions. The earliest works comprise structure elucidation of ammonium sulfidotungstate,<sup>[2]</sup> followed by the derivatives of the larger alkali metals rubidium,<sup>[3]</sup> cesium<sup>[4]</sup> and two closely related modifications of  $Cu_2[WS_4]$ <sup>[5]</sup> as coinage metal representatives. Furthermore, a verified plethora of alkylated and arylated ammonium salts according to  $(R_{1-4}NH_{3-0})_2[WS_4]$  (e.g.  $R = \text{ethyl, butyl, methylbenzyl, etc.}$ ) are known as well as sulfidotungstates with mono- and divalent organic cations have been investigated by the group of Srinivasan (e.g. bis(piperazine-1-ium) tetrasulfidotungstate, piperazine-dium tetrasulfidotungstate, etc.).<sup>[8]</sup> Surprisingly, no sulfidotungstates of the alkaline earth metals according to  $AE[WS_4]$  have been investigated so far, while their oxido-congeners not only occur naturally but represent the main source for tungsten on this planet. The

same is true, albeit not that surprising, for rare-earth metal sulfidotungstates with compositions related to the respective oxidotungstates or their derivatives. These classes of compounds, however, should show some potential for optical applications, due to two interesting properties. First, the ligand-to-metal charge-transfer (LMCT), present in complex sulfidotungstate entities is strongly shifted towards regions of lower energies, compared to the respective oxidotungstates,<sup>[9]</sup> which can easily be seen by the yellow to red colors of the materials containing sulfidotungstate entities, in contrast to the mostly colorless oxidotungstate ones. Second, other than many sulfidoanions, such as sulfidophosphates,<sup>[10]</sup> -silicates,<sup>[11]</sup> etc.,  $[WS_4]^{2-}$  units do not undergo complete or superficial hydrolysis, thus remaining stable to atmospheric conditions. In attempts to remedy the lack of rare-earth metal sulfidotungstates in solid-state reactions utilizing potassium and sodium polysulfides, such as  $K_2S_3$ <sup>[12]</sup> or  $Na_2S_6$ <sup>[13]</sup> as reactive flux, respectively, the title compounds emerged as by-products. Further attempts to synthesize both compounds as single phase products have been successful in case of  $K_2[WS_4]$ , but not for  $Na_2[WS_4] \cdot 4H_2O$ .

## Results and Discussion

### Crystal Structure of $K_2[WS_4]$

$K_2[WS_4]$  crystallizes isotypic to the sulfidotungstates of the larger alkali metals  $Rb_2[WS_4]$ <sup>[3]</sup> and  $Cs_2[WS_4]$ <sup>[4]</sup> as well as the ammonium derivative  $(NH_4)_2[WS_4]$ <sup>[2]</sup> and the sulfidomolybdates  $A_2[MoS_4]$  with  $A = K, Rb, Cs$ .<sup>[14]</sup> Its orthorhombic crystal structure was first mentioned in 2001<sup>[15]</sup> and reported in 2009<sup>[16]</sup> in detail. It comprises two crystallographically distinguishable  $K^+$  cations, coordinated by five and six sulfidotungstate tetrahedra, respectively, yielding a coordination number of nine for  $(K1)^+$

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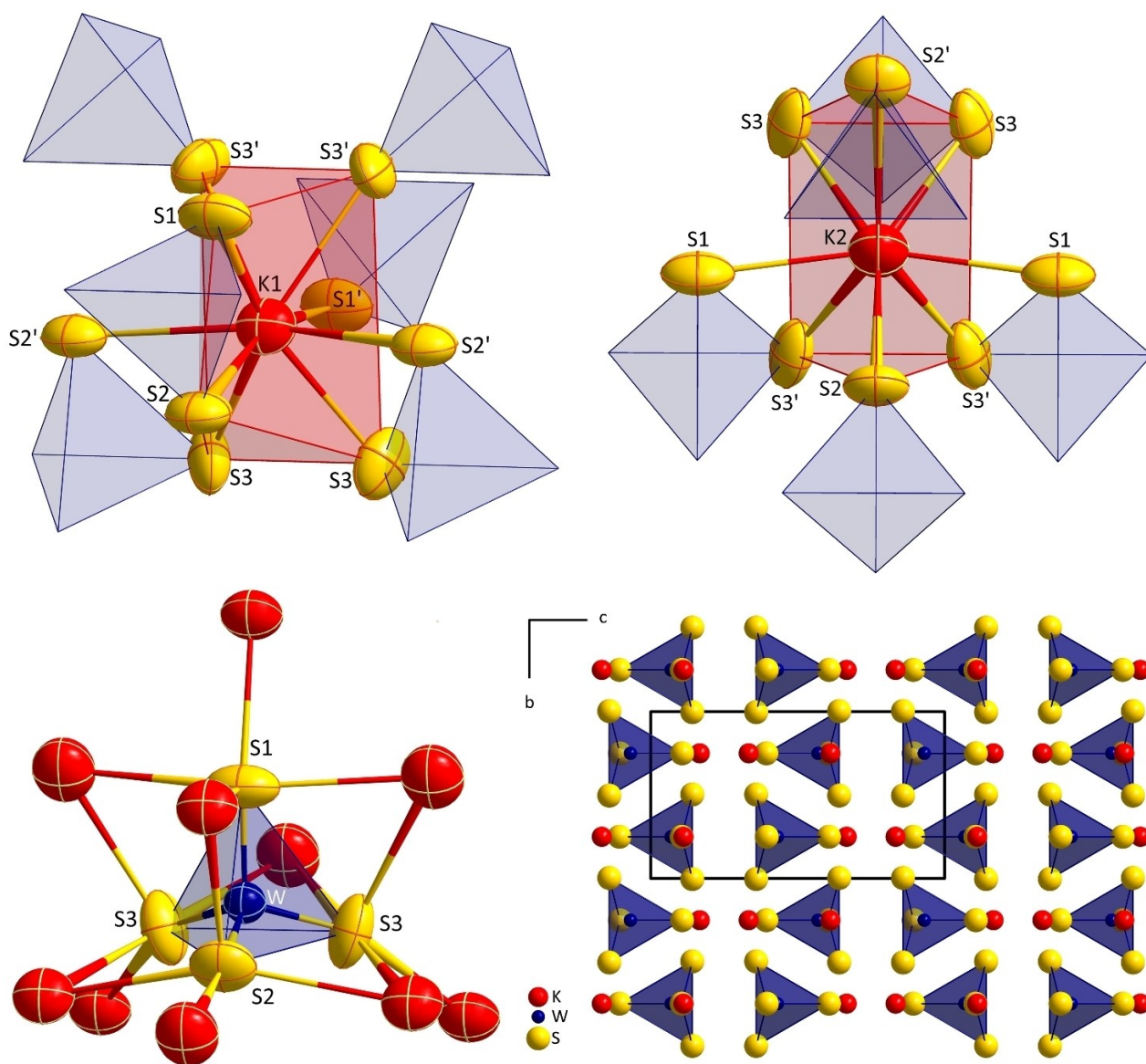
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and eight for  $(K2)^+$ , each in the shape of distorted trigonal prisms with three caps in the former (Figure 1, *top left*) and two in the latter case (Figure 1, *top right*). The  $[WS_4]^{2-}$  thereby function both as bidental and vertex coordinating ligands.

The interatomic distances and angles (see Table 1) are in good agreement with the data previously published for  $K_2[WS_4]$ .<sup>[16]</sup> The  $[WS_4]^{2-}$  entities are surrounded by ten  $K^+$  cations, sharing common vertices and edges, but no faces (Figure 1, *bottom left*). The arrangement of the aforementioned building blocks is isotopic to the  $\beta$ - $K_2SO_4$  or *arcanite* structure as depicted in Figure 1, *bottom right*.<sup>[18]</sup>

### Crystal structure of $Na_2[WS_4] \cdot 4H_2O$

In the monoclinic crystal structure of the novel  $Na_2[WS_4] \cdot 4H_2O$ , two crystallographically distinguishable sodium cations are found. Both exhibit a coordination number of six, created by two sulfide anions and four water molecules in the shape of more ( $Na2$ ) or less ( $Na1$ ) distorted octahedra (Figure 2, *top left* and *middle*). While for  $(Na1)^+$  the two  $(S2)^{2-}$  ligands are trans-oriented, representing common vertices with the  $[WS_4]^{2-}$  tetrahedra, the  $(S1)^{2-}$  anions around  $(Na2)^+$  constitute a common edge with the coordinating sulfidotungstate unit and are thus cis-oriented. The interatomic distances between sodium and sulfur show values between 294 and 298 pm (Table 2), which correspond very well to those of other sodium



**Figure 1.** Coordination environments around the  $(K1)^+$  (*top left*) and the  $(K2)^+$  cations (*top right*) as well as around the  $[WS_4]^{2-}$  tetrahedra (*bottom left*) in the crystal structure of  $K_2[WS_4]$  (ellipsoid representation at 95% probability), together with a view at the expanded unit cell along [100] (*bottom right*)

**Table 1.** Motifs of mutual adjunction,<sup>[17]</sup> interatomic distances, and selected bond angles in the crystal structure of K<sub>2</sub>[WS<sub>4</sub>].

Atom	S1	S2	S3	CN
K1	2/2	3/3	4/2	9
<i>d</i> /pm	1×313.94(15) 1×321.13(14)	1×336.36(15) 2×356.0(3)	2×333.33(12) 2×343.48(11)	
K2	2/2	2/2	4/2	8
<i>d</i> /pm	2×351.4(3)	1×335.43(14) 1×370.88(15)	2×342.00(13) 2×353.02(13)	
W	1/1	1/1	2/1	4
<i>d</i> /pm	1×217.94(11)	1×219.32(11)	2×217.83(8)	
//deg	–S2: 1×111.29(4) –S3: 2×108.98(3)	–S3: 2×109.95(3)	–S3: 1×107.61(5)	
CN	5	6	5	

**Table 2.** Interatomic distances and selected bond angles in the crystal structure of Na<sub>2</sub>[WS<sub>4</sub>]·4H<sub>2</sub>O

distance/angle	value	distance/angle	value
Na1–O1 (2×)	238.7(3) pm	W–S1 (2×)	218.06(10) pm
Na1–O2 (2×)	241.5(4) pm	W–S2 (2×)	220.03(10) pm
Na1–S2 (2×)	294.53(11) pm	S1–W–S2	110.19(6)°
Na2–O1 (2×)	242.0(4) pm	S1–W–S2 (2×)	108.90(4)°
Na2–O2 (2×)	239.1(3) pm	S1–W–S2 (2×)	109.44(4)°
Na2–S1 (2×)	297.8(2) pm	S2–W–S2	109.94(6)°
O1–H1A	89(2) pm	O2–H2A	89(2) pm
O1–H1B	89(2) pm	O2–H2B	89(2) pm
H1A–O1–H1B	99(5)°	H2A–O2–H2B	108(5)°
Intralayer hydrogen bonds		Interlayer hydrogen bonds	
H1A ... S2	242(2) pm	H1B ... S2	262(2) pm
O1–H1A ... S2	169.6(2)°	O1–H1B ... S2	149.4(2)°
H2B ... S1	260(2) pm	H2A ... S2	282(2) pm
O2–H2B ... S1	171.5(1)°	O2–H2A ... S2	138.1(2)°
		H2A ... S1	281(2)
		O2–H2A ... S1	140.2(2)°

compounds with complex sulfidoanions, such as Na<sub>3</sub>[VS<sub>4</sub>] with  $d(\text{Na}^+ \cdots \text{S}^{2-}) = 283\text{--}299$  pm.<sup>[19]</sup> The same is true for the distances between Na<sup>+</sup> and H<sub>2</sub>O, ranging from 238 to 242 pm (Table 2), which are in good agreement to the water containing sodium oxidotungstate Na<sub>2</sub>[WO<sub>4</sub>]·2 H<sub>2</sub>O for example, with the latter showing values from 231 to 245 pm.<sup>[20]</sup> The sulfidotungstate tetrahedra themselves display only a slight distortion with angles of 108.9° to 110.2° with a 7 % deviation from the ideal tetrahedral angle (Figure 2, *top right*). The W<sup>6+</sup>–S<sup>2-</sup> bond lengths reside between 218 and 220 pm (Table 2) and are thus similar to those found in the previously described K<sub>2</sub>[WS<sub>4</sub>]. The polyhedra around the sodium cations are connected to one another via common edges resulting in zig-zag-chains along the crystallographic *c* axis, which are connected by the W<sup>6+</sup> cations to form layers parallel to the *bc* plane (Figure 2, *bottom left*). Furthermore, there are O–H...S hydrogen bonds detectable within the aforementioned layers (dashed bonds in Figure 2).

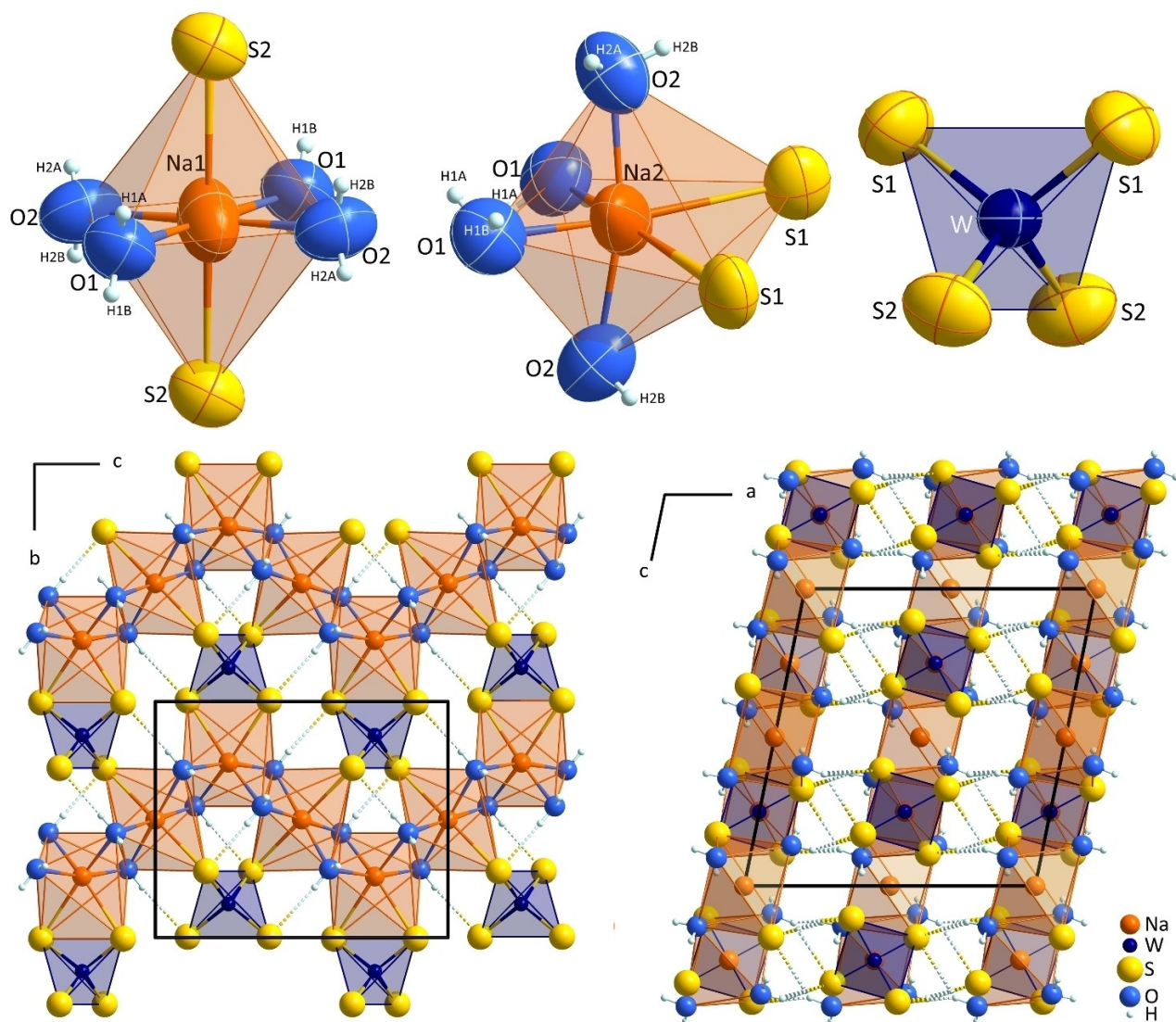
These types of bonds are not uncommon and especially in organic compounds and rather well investigated since the

1960s.<sup>[21]</sup> Here interactions between S2 and O1 (via H1A) as well as between S1 and O2 (via H2B) are discussed with distances according to  $d(\text{S}^{2-} \cdots \text{H1A}^+) \approx 243$  and  $d(\text{S1}^{2-} \cdots \text{H2B}^+) \approx 260$  pm (Note: The O–H distances were all refined with a fixed distance of 89 pm) and the respective S...H–O angles residing between 169–170° and. The layers seen in Figure 2, *bottom left*, exhibit the complete composition of the title compound Na<sub>2</sub>[WS<sub>4</sub>]·4H<sub>2</sub>O and are thus electroneutral. They are stacked along [100] with a shift of + $\frac{1}{2}$  in *b* direction from layer to layer with the interactions between those sheets being accomplished merely by O–H...S hydrogen bonds. Compared to the intralayer ones, the interlayer bonds are considerably longer,  $d(\text{S}^{2-} \cdots \text{H}^+) = 262\text{--}282$  pm, and the arrangement shows lower (O–H...S) angles with values between 138 and 149°. Hence, according to hydrogen bridges being stronger the more linear they are,<sup>[22]</sup> the interactions between the previously described layers have to be rather weak. On the other hand, both S2 and H2A participate in two hydrogen bonds, respectively, so that a bifurcated arrangement of those interactions at the particular atom is detected (Figure 2, *bottom right*, dashed bonds), holding the layers in a position that the hydrogen bond lengths are retained at their minima, thus preventing them from displacing against each other. This phenomenon is also detected macroscopically since these crystals are not very sensitive against mechanical manipulation.

These hydrogen bonds also show a small effect on the W<sup>6+</sup>–S<sup>2-</sup> bond lengths: S2, taking part in three hydrogen bonds (one of them being also the shortest hydrogen bond found in the crystal structure) is about 2 pm farther away from the tungsten hexacation than S1, which is only participating in two of the longer hydrogen bonds. This effect is also observed in several alkylated ammonium sulfidotungstates, e.g. [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[WS<sub>4</sub>],<sup>[16]</sup> in which the sulfide anions showing the longest W<sup>6+</sup>–S<sup>2-</sup> bond length are partaking in more and shorter hydrogen bonds than those exhibiting a shorter distance to W<sup>6+</sup>.

### Raman and infrared spectroscopy

Single crystal Raman spectra were collected for both compounds, utilizing a green laser at  $\lambda = 532$  nm for K<sub>2</sub>[WS<sub>4</sub>] and a red one at  $\lambda = 638$  nm for Na<sub>2</sub>[WS<sub>4</sub>]·4H<sub>2</sub>O. Raman investigations of sulfidotungstates have been carried out in the past, especially the group around Müller performed thorough Raman and IR investigations of complex sulfidometalates, both in solution and in the solid state.<sup>[23]</sup> The spectra of the two title compounds show their strongest peak at 485 cm<sup>-1</sup> (Figure 3) each, which corroborates with the findings of the Müller group to the symmetric stretching vibrations of the [WS<sub>4</sub>]<sup>2-</sup> tetrahedra. The antisymmetric stretching vibrations are visible at 455 cm<sup>-1</sup>, with a slight shoulder at 469 cm<sup>-1</sup> in case of K<sub>2</sub>[WS<sub>4</sub>]. These vibrations are also visible in the spectrum of Na<sub>2</sub>[WS<sub>4</sub>]·4H<sub>2</sub>O, however, both of them as shoulders at the band of the symmetric stretching vibrations.



**Figure 2.** Top: Coordination environments around the  $(\text{Na}1)^+$  (left) and the  $(\text{Na}2)^+$  cations (middle) as well as the  $[\text{WS}_4]^{2-}$  tetrahedra (right) in the crystal structure of  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$  (ellipsoid representation at 95% probability); bottom:  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$  layers situated parallel to the  $bc$  plane (left) and arrangement of those layers represented in an expanded unit cell, viewed along  $[010]$  (right) with special emphasis on the  $\text{O}-\text{H}\cdots\text{S}$  hydrogen bonds (dashed lines).

The deformation vibrations are visible in the range between  $175$  and  $200\text{ cm}^{-1}$  albeit not very well resolved, which is also in good agreement with previous findings.<sup>[23]</sup>

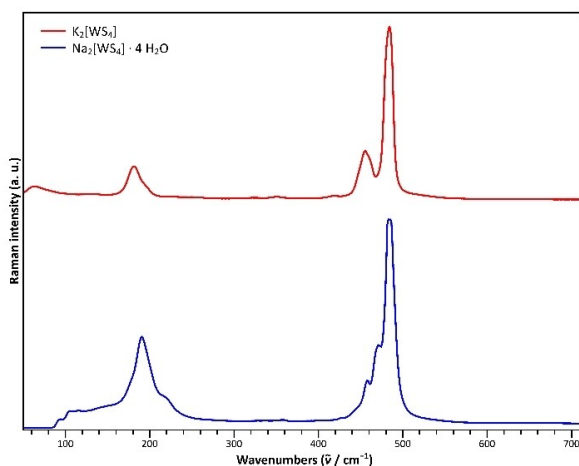
Since  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$  was not available as single phase material, an IR spectrum of a crystalline powder was only measured for  $\text{K}_2[\text{WS}_4]$  (Figure 4).

Here the antisymmetric stretching vibrations are visible as strongest peak with a maximum at about  $453\text{ cm}^{-1}$  and a shoulder of the symmetric one at  $485\text{ cm}^{-1}$ , which corresponds to the findings by Srinivasan et. al.<sup>[16]</sup> The vibration bands at  $197$  as well as the double peak at  $175$  and  $179\text{ cm}^{-1}$  can be assigned to the deformation modes of the  $[\text{WS}_4]^{2-}$  tetrahedra.<sup>[23]</sup> The other bands visible in the spectrum cannot be related to vibrations of the sulfidotungstate tetrahedra and are assumed to be phononic modes.

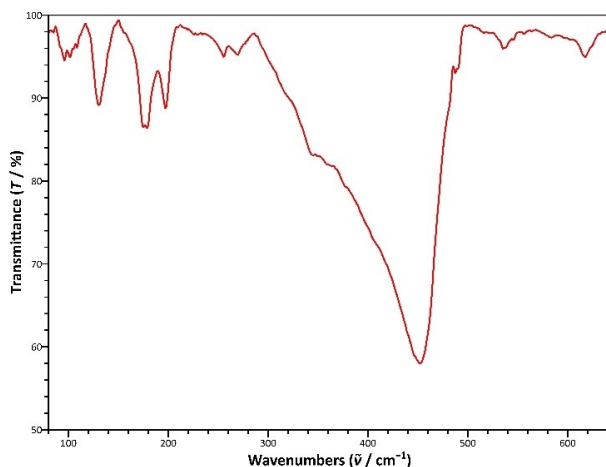
#### Diffuse reflectance spectroscopy

The optical band gap of single-phase  $\text{K}_2[\text{WS}_4]$  was determined by diffuse reflectance spectroscopy (DRS) and the application of the *Kubelka-Munk* function to the measured spectrum (Figure 5).<sup>[24]</sup> The intersection of the tangents to the baseline and to the steepest slope of the spectrum determines the optical band gap, which resulted in a value of  $2.30\text{ eV}$  ( $539\text{ nm}$ ) and corresponds well to the red-orange color of the crystals.

This band gap results from the  $\text{S}^{2-} \rightarrow \text{W}^{6+}$  ligand-to-metal charge transfer (LMCT), which is considerably shifted towards lower energies, compared to the respective tetrahedral oxidotungstates, in which the LMCT transition occurs at about  $290\text{ nm}$ .<sup>[25]</sup>



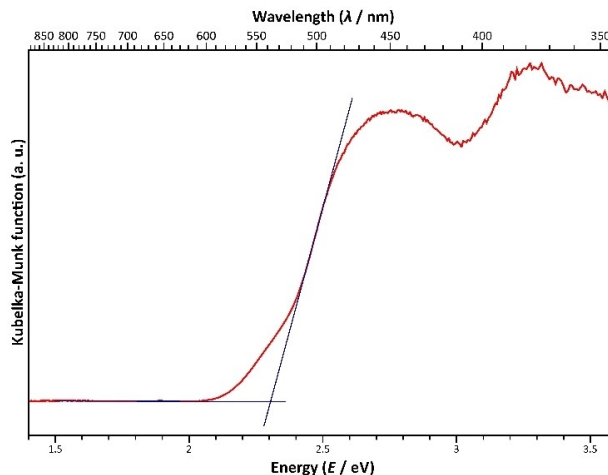
**Figure 3.** Single crystal Raman spectra of  $K_2[WS_4]$  (top, red line) and  $Na_2[WS_4] \cdot 4H_2O$  (bottom, blue line)



**Figure 4.** IR spectrum of  $K_2[WS_4]$

## Conclusions

The synthesis and characterization of the two alkali metal sulfidotungstates  $K_2[WS_4]$  and  $Na_2[WS_4] \cdot 4H_2O$ , which emerged as by-products during syntheses attempts of two different rare-earth metal sulfidotungstates are, albeit not desired, helpful as important model compounds for future research in the direction of alkaline earth or rare-earth metal sulfidotungstates. Two points are strongly proven, firstly the  $[WS_4]^{2-}$  units are stable against hydrolysis, as seen in the sodium compound, which was clearly exposed to water, nonetheless displaying intact sulfidotungstate tetrahedra. Secondly, the optical band gap of these entities shows a red shift of about 250 nm with respect to the analogous oxidotungstates, which turns compounds comprising these units into interesting host materials for luminescence applications with a sensitizer group absorbing light in the visible range of the electromagnetic spectrum.



**Figure 5.** Diffuse reflectance spectrum of  $K_2[WS_4]$  with the appropriate tangents to determine the onset point of the optical band gap.

## Experimental Section

**Synthesis of the alkali metal polysulfides:** The synthesis of sodium and potassium polysulfides, which were used as reactive flux, comprised 1 g potassium (K, purity, 99.95%, ChemPur, Karlsruhe, Germany) and 0.82 g sulfur (S, purity: 99.999%, Fluka, Buchs, Switzerland) or 1 g sodium (Na, purity > 97%, Riedel-de-Haën, Seelze, Germany) and 2.1 g sulfur, respectively. The alkali metal and the sulfur were weighed into a pressure-tight test tube, which was subsequently inserted into a brass container and closed with a valve. The arrangement was cooled to  $-78^\circ\text{C}$  by means of an ethanol/dry ice mixture and with the help of a tensi-eudiometer<sup>[26]</sup> the test tube was filled with liquid ammonia ( $NH_3$ , 99.999%, Linde, Darmstadt, Germany) to half of its volume. The blue solution changes color to orange in the course of four days. After that period, the mixture has been brought to room temperature and the ammonia was removed. In both syntheses, orange colored products were characterized by means of powder diffraction and absorption spectroscopy. In case of the potassium product, a mixture of  $K_2S_3$  and  $K_2S_4$  was determined, while the main product containing sodium was  $Na_2S_6$  with traces of  $NaNH_2$  as by-product.

**Synthesis of  $K_2[WS_4]$ :** Single crystals of  $K_2[WS_4]$  were obtained as a by-product in unsuccessful syntheses attempts to obtain a holmium sulfidotungstate, utilizing potassium polysulfide as reactive flux. Single-phase  $K_2[WS_4]$  was obtained by the reaction of 131 mg of the pre-synthesized potassium polysulfide with 92 mg of tungsten (W, purity: 99.9%, ChemPur, Karlsruhe, Germany) in graphitized silica ampoules. The fused containers were heated to  $700^\circ\text{C}$  (rate  $100^\circ\text{C}/\text{h}$ ) and this temperature was held for four days before cooling to  $500^\circ\text{C}$  in four days as well and subsequently the mixture was cooled to room temperature. The reaction yielded a red-orange coloured crystalline powder, stable to atmospheric conditions and in sufficient quality for both single crystal and powder X-ray diffraction.

**Synthesis of  $Na_2[WS_4] \cdot 4H_2O$ :** Single crystals of  $Na_2[WS_4] \cdot 4H_2O$  were obtained as by-product of a synthesis attempt to yield neodymium sulfidotungstate, in which sodium polysulfide was used as reactive flux. 102 mg of the polysulfide was weighed into a graphitized silica ampoule together with 69 mg of tungsten and 36 mg of neodymium (Nd, purity: 99.9%, ChemPur, Karlsruhe, Germany). After fusing the container, the temperature program

mentioned in the previous section was applied. After opening the ampoule, the crude product underwent hydrolysis, however, after allowing the water to evaporate within 2 days, orange-yellow single crystals of  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$  were identified, which showed sufficient quality for single crystal X-ray diffraction.

**Single-crystal structure determination:** Intensity data sets for  $\text{K}_2[\text{WS}_4]$  and  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$  were collected with a STOE StadiVari diffractometer (Stoe & Cie. Darmstadt, Germany), equipped with a Ag microfocuss X-ray tube (Table 3). The hydrogen atoms in the structure of  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$  were found in difference Fourier data and refined with a fixed distance of 89 pm as well as isotropic displacement parameters of 1.3 times the parameter of the respective oxygen atom, they were assigned to.

Further information on the crystal structures of the title compounds can be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: <https://www.ccdc.cam.ac.uk/structures/> by quoting the deposition numbers CSD-2173854 for  $\text{K}_2[\text{WS}_4]$  and CSD-2183853 for  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$ .

**Powder X-ray diffraction:** A powder pattern of  $\text{K}_2[\text{WS}_4]$  was recorded on a Stoe StadiP powder diffractometer (Stoe & Cie, Darmstadt, Germany), equipped with a position sensitive detector (PSD), utilizing germanium-monochromatized  $\text{Cu-K}\alpha_1$  radiation ( $\lambda = 154.06$  pm). LeBail profile fitting was conducted with the help of the FullProf program suite (Figure 6),<sup>[31]</sup> in which the phase purity of

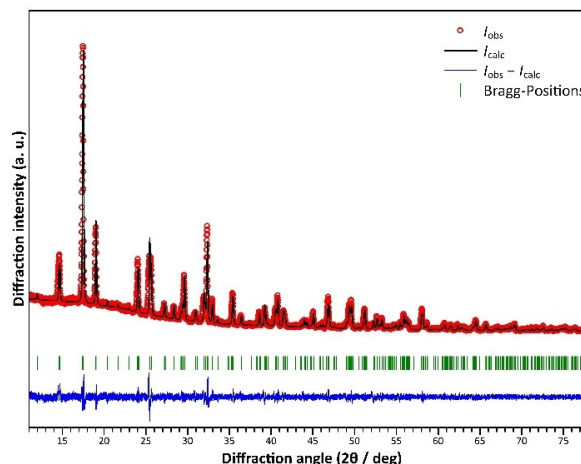


Figure 6. Profile-fitted powder pattern of  $\text{K}_2[\text{WS}_4]$

the compound within the limitations of powder X-ray diffraction was determined.

**Raman spectroscopy:** Single crystal Raman spectra of the title compounds were recorded with the help of a Horiba Xplora spectrometer (Kyoto, Japan) by using a laser device with a wavelength of  $\lambda = 532$  nm for  $\text{K}_2[\text{WS}_4]$  and  $\lambda = 638$  nm for  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$

**Infrared spectroscopy:** The infrared spectrum of  $\text{K}_2[\text{WS}_4]$  was recorded with a Bruker Vertex 70v FT-IR spectrometer (Ettlingen, Germany) equipped with an evacuable ATR unit and a DAL TGS detector, providing a measuring range from 10 to  $700\text{ cm}^{-1}$ .

**Diffuse reflectance spectroscopy:** The diffuse reflectance spectrum of  $\text{K}_2[\text{WS}_4]$  was measured by using a J & M Tidas UV/Vis/NIR spectrophotometer (Essingen, Germany), equipped to collect diffusely scattered radiation. Barium sulfate was used as standard white reference. The *Kubelka-Munk*-function<sup>[24]</sup> was applied to the collected data for obtaining optical band gap information.

**Table 3.** Crystallographic data of  $\text{K}_2[\text{WS}_4]$  and  $\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$ , measured on a Stoe StadiVari diffractometer utilizing  $\text{Ag-K}\alpha$  radiation ( $\lambda = 56.083$  pm); corrections for background, polarization and Lorentz factors were applied as well as a multi-scan absorption correction with the help of the program X-Red32<sup>[27]</sup> and scaling of reflection intensities with the program LANA.<sup>[28]</sup> Structure solution was performed with the SHELX-2018 program package,<sup>[29]</sup> with scattering factors according to International Tables, Vol. C.<sup>[30]</sup>

Compound	$\text{K}_2[\text{WS}_4]$	$\text{Na}_2[\text{WS}_4] \cdot 4\text{H}_2\text{O}$
Crystal system	orthorhombic	monoclinic
Space group	<i>Pnma</i>	<i>C2/c</i>
Formula units, Z	4	
Lattice parameters:		
<i>a</i> /pm	935.10(3)	1098.08(4)
<i>b</i> /pm	694.22(2)	904.46(3)
<i>c</i> /pm	1221.85(4)	1144.27(4)
$\beta$ /deg	90	101.577(3)
Crystallographic density, $\rho_c$ / $\text{g} \cdot \text{cm}^{-3}$	3.268	2.566
Molar volume, $V_m/\text{cm}^3 \cdot \text{mol}^{-1}$	119.42	167.62
<i>F</i> (000)	704	800
Measurement range $\pm h/\pm k/\pm l$	14/11/21	18/15/19
Diffraction angle $\theta_{\min}-\theta_{\max}$	2.164 –28.903	2.231 –27.857
Absorption coefficient, $\mu/\text{mm}^{-1}$	8.841	5.987
Reflections measured/unique	25027/2252	24979/2695
Number of parameters	41	65
$R_{\text{int}}/R_\sigma$	0.046/0.027	0.103/0.070
$R_1$ for <i>n</i> reflections with $ F_o  \geq 4\sigma(F_o)$	0.022, <i>n</i> = 1561	0.036, <i>n</i> = 1936
$R_1/wR_2$ for all reflections	0.047/0.043	0.066/0.059
Goodness of Fit, <i>S</i>	0.982	0.889
Extinction, <i>g</i>	0.00085(15)	–
Residual electron density, $\rho_{\text{min}}/\rho_{\text{max}}/10^{-6} \text{ e}^- \cdot \text{pm}^{-3}$	–1.12/1.00	–1.20/1.37

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** sulfidotungstates · thiotungstates · alkali metal · crystal structure · spectroscopy

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