**Supporting information**


**Synthesis and structure of quasi-one-dimensional niobium tetrasulfide NbS$_4$**

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***Chemical procedures.*** The starting niobium chalcogenides were synthesized from the elements in evacuated quartz ampoules. The ratios of the elements were stoichiometric or close to stoichiomentric. The crystalline phase purity of the niobium chalcogenides ($NbS_2$, $NbS_3$, $Nb_2Se_3$, $NbSe_2$, $NbSe_3$, $NbTe_2$) were checked by XRPD after their synthetic procedures. Only the target compounds were detected.

***Synthesis of NbS₂:*** niobium powder (11.834g 128.5mmol) and sulfur (8.345g 260.3mmol) was evacuated and sealed in a quartz ampule of volume 40 ml. Excess of sulfur was taken for providing pressure of vapors ca. 7 atm at temperature of synthesis. The ampule was heated up to 900°C in 10 h, kept at 900°C for 40 h, and quenched in water down to the room temperature (appropriate safety facilities should be used at the ampule quenching). The ampule was opened, and excess sulfur was pumped out in dynamic vacuum at 200°C.

***Synthesis of NbS₃:*** niobium powder (9.826g 105.8mmol) and sulfur (10.50g 327.5mmol) was evacuated and sealed in a quartz ampule of volume 50 ml. Excess of sulfur was taken for providing pressure of vapors ca. 6 atm at temperature of synthesis, and also to prevent dissociation of $NbS_3$ to $NbS_2$ and S. The ampule was heated up to 600°C in 24 h, kept at 600°C for 150 h. The ampule was opened, and excess sulfur was pumped out in dynamic vacuum at 200°C. $NbS_3$ was used in the synthesis of $Nb_{1.14}S_2$.

***Synthesis of Nb₂Se₃:*** equivalent amounts of Nb and Se elements, along with a few iodine crystals used as a transport agent, were placed in a quartz tube, evacuated, sealed, heated up to 1100°C at a rate of 45 C/h and kept at 1100°C for 90 h in order to allow the reaction of $Nb_2Se_3$ formation to proceed completely. The quartz tube was cooled down by quenching in an iced water bath (to avoid phase transformation of $Nb_2Se_3$ into iso-stoichiometric intercalated phase $Nb_{1.33}Se_2$).

***Synthesis of NbSe₂:*** niobium powder (3.704g 39.87mmol) and selenium pellets (6.296g 79.73mmol) was evacuated and sealed in a quartz ampule of volume 50 ml. The ampule was heated up to 800°C in 10 h, kept at 800°C for 30 h.

***Synthesis of NbSe₃:*** niobium powder (9.826g 105.8mmol) and selenium pellets (25.86 g, 327.5 mmol) was evacuated and sealed in a quartz ampule of volume 50 ml. The ampule was heated up to 400°C in 24 h, and then further heated 700°C ($NbSe_3$) with speed 1°/min. The ampule kept for 7 days at 700°C, and after that was cooled down with the furnace. The product $NbSe_3$ was good crystallized, in part as long fibrous crystals. After opening, excess of selenium were evacuated under dynamic vacuum at 350°C.

***Synthesis of NbTe₂:*** niobium powder (2.669 g 28.73 mmol) and tellurium (7.331 g 57.45 mmol) was evacuated and sealed in a quartz ampule of volume 50 ml. The ampule was heated up to 800°C in 10 h, kept at 800°C for 30 h.
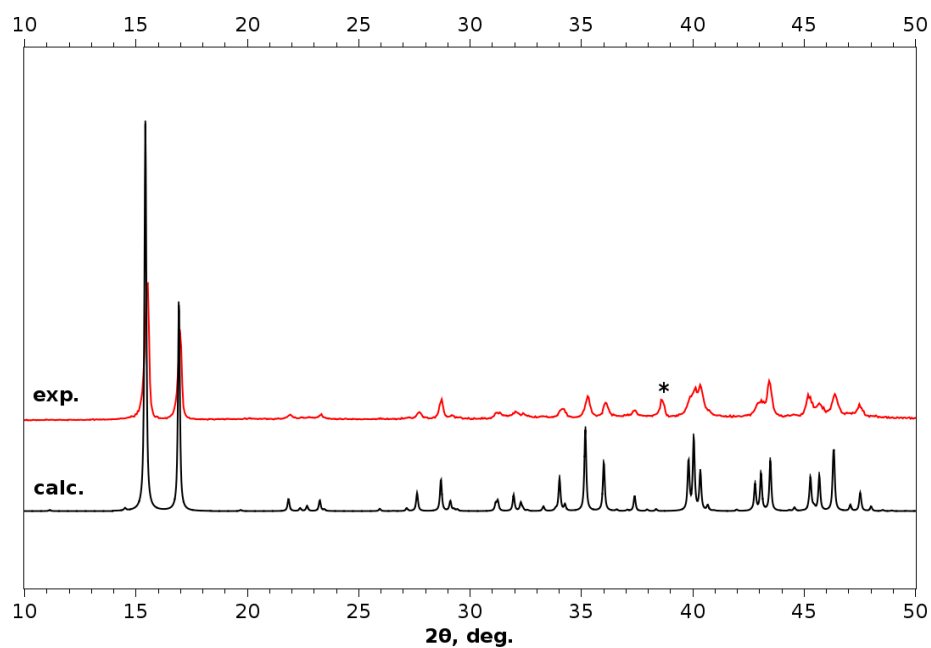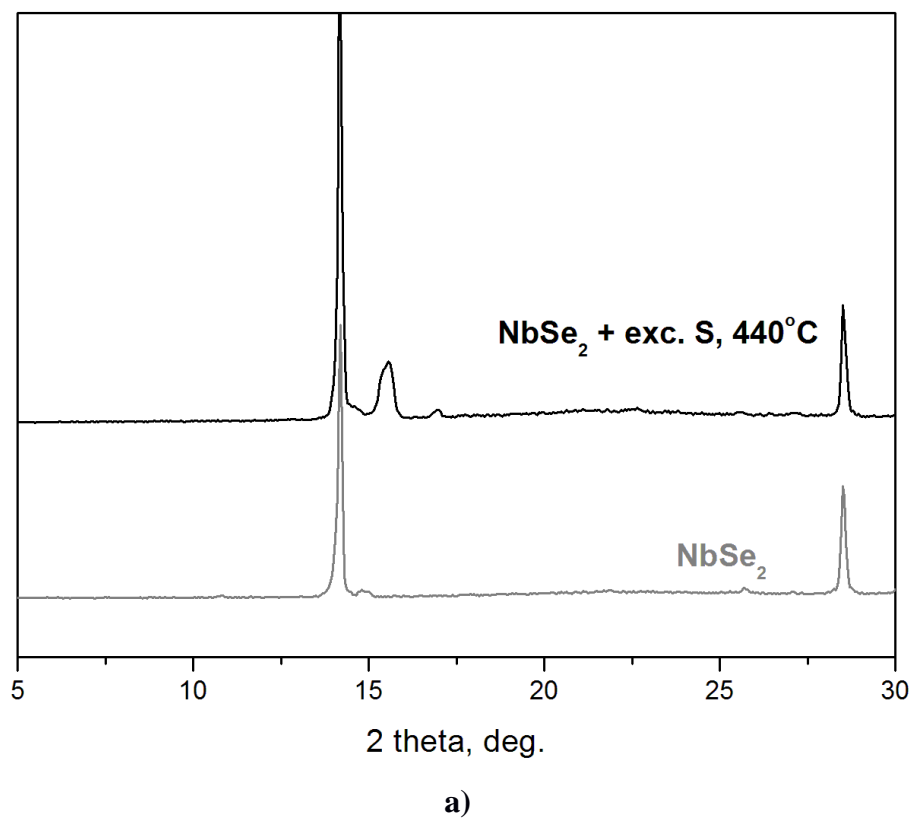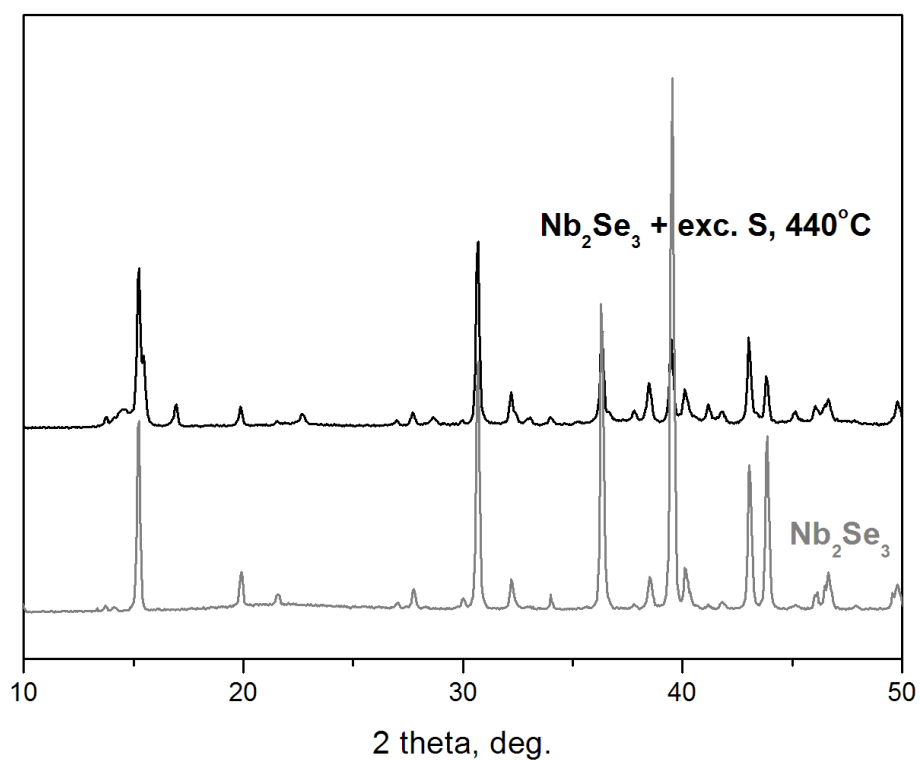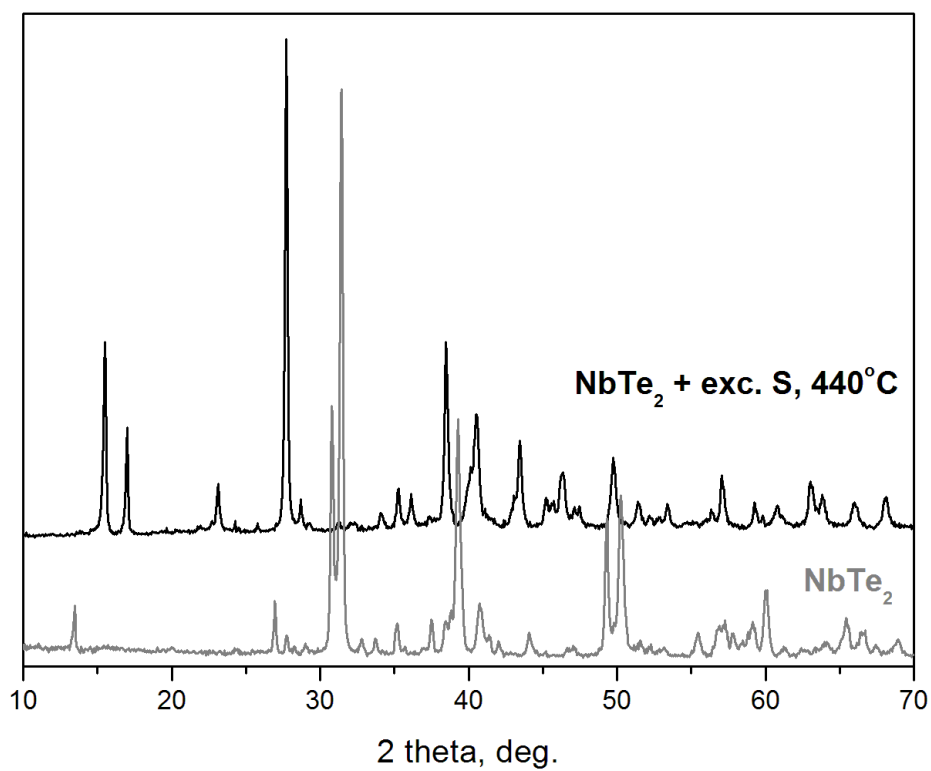
Figure S1.  Experimental (synthesized from Nb and S) and calculated XRD patterns for $NbS_4$. The starred peak belongs to metal niobium.



a)

Figure S2. Experimental powder diffractograms of reactions products of $NbSe_2$ (a), $Nb_2Se_3$ (b) and $NbTe_2$ (c) with excess sulfur (upper black lines).
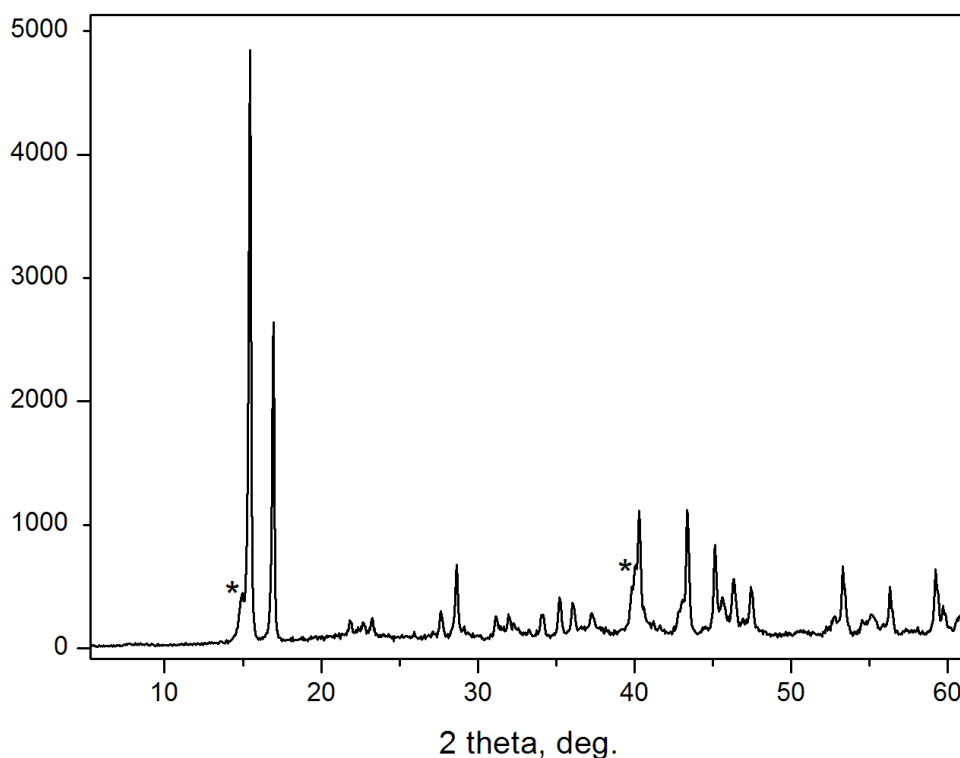
Figure S3. XRPD pattern of the product of reaction of $Nb_{1.14}S_2$ and excess sulfur at 440°C. The starred peaks belong to $NbS_2$.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2110999 and can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

Table S1. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $NbS_4$ at 150K. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | $x$ | $y$ | $z$ | U(eq) |
|------|-----|-----|-----|-------|
| Nb01 | 6327.5(2) | 7514.8(2) | 3825.6(4) | 5.74(7) |
| S002 | 4688.2(6) | 8492.4(6) | 4639.4(11) | 8.57(14) |
| S003 | 4859.3(6) | 6532.3(6) | 4798.6(11) | 8.82(15) |
| S004 | 7532.9(6) | 5593.9(6) | 4439.3(12) | 9.48(15) |
| S005 | 7758.3(6) | 6916.0(6) | 2427.6(11) | 8.78(14) |

Table S2. Anisotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $NbS_4$ at 150K. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|----------|----------|----------|----------|----------|----------|
| Nb01 | 4.59(11) | 6.55(11) | 5.92(11) | -0.03(10) | 1.80(8) | 0.42(10) |
| S002 | 7.5(3) | 9.4(3) | 8.4(3) | -1.3(3) | 2.6(3) | 0.6(2) |
| S003 | 7.1(3) | 10.3(3) | 8.9(3) | 2.2(3) | 2.8(3) | -0.2(2) |
| S004 | 9.1(3) | 7.1(3) | 11.9(4) | -0.2(3) | 3.4(3) | 0.8(2) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|------|------|------|------|------|------|
| S005 | 6.8(3) | 12.3(3) | 7.5(3) | -1.1(3) | 3.0(3) | 0.8(3) |

Table S3. Bond Lengths in the X-ray crystal structure of $NbS_4$.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Nb01 | Nb01[1] | 2.8959(6) | Nb01 | S005[1] | 2.4983(8) |
| Nb01 | Nb01[2] | 3.2775(7) | Nb01 | S005 | 2.4954(8) |
| Nb01 | S002[2] | 2.4947(8) | S002 | Nb01[2] | 2.4947(8) |
| Nb01 | S002 | 2.6275(8) | S002 | S003 | 2.0598(9) |
| Nb01 | S003 | 2.4901(8) | S003 | Nb01[2] | 2.6259(8) |
| Nb01 | S003[2] | 2.6259(8) | S004 | Nb01[1] | 2.5007(8) |
| Nb01 | S004 | 2.4927(8) | S004 | S005 | 2.0645(10) |
| Nb01 | S004[1] | 2.5007(8) | S005 | Nb01[1] | 2.4983(8) |

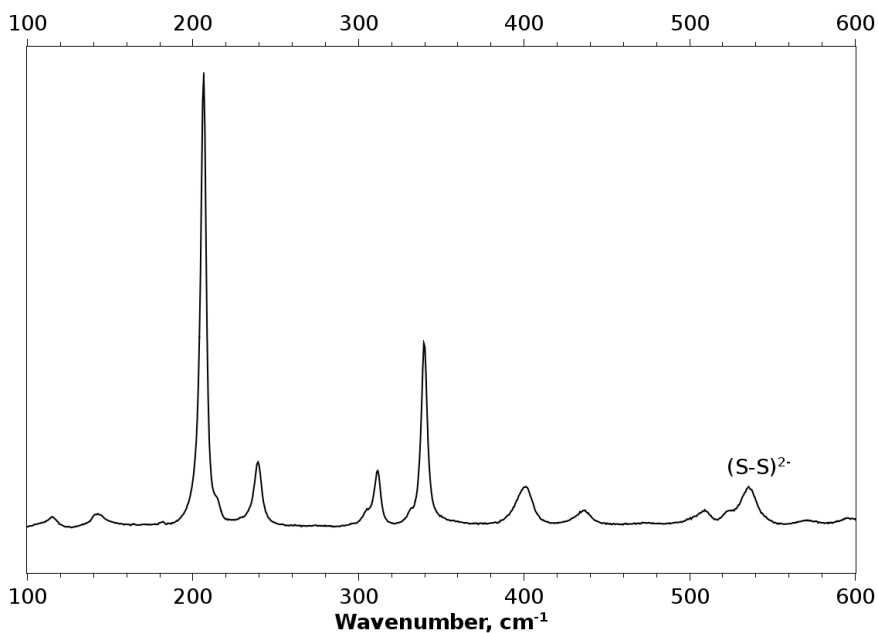[1]3/2-X,3/2-Y,1-Z; [2]1-X,+Y,1/2-Z



Figure S4. Raman spectrum of $NbS_4$ powder.

Table S4. The most important bond lengths of $VS_4$ in comparison with $NbS_4$

|  | $NbS_4$ (exp., this work) | $NbS_4$ (calcd., this work) | $VS_4$ (exp. [8]) |
|------|------|------|------|
| Cell parameters, sp. gr. *C2/c* | $a = 13.126(2)$ Å, $b = 10.4538(14)$ Å, | $a = 13.347$ Å, $b = 10.367$ Å, | $a = 12.7131(6)$, $b = 10.3532(6)$, |

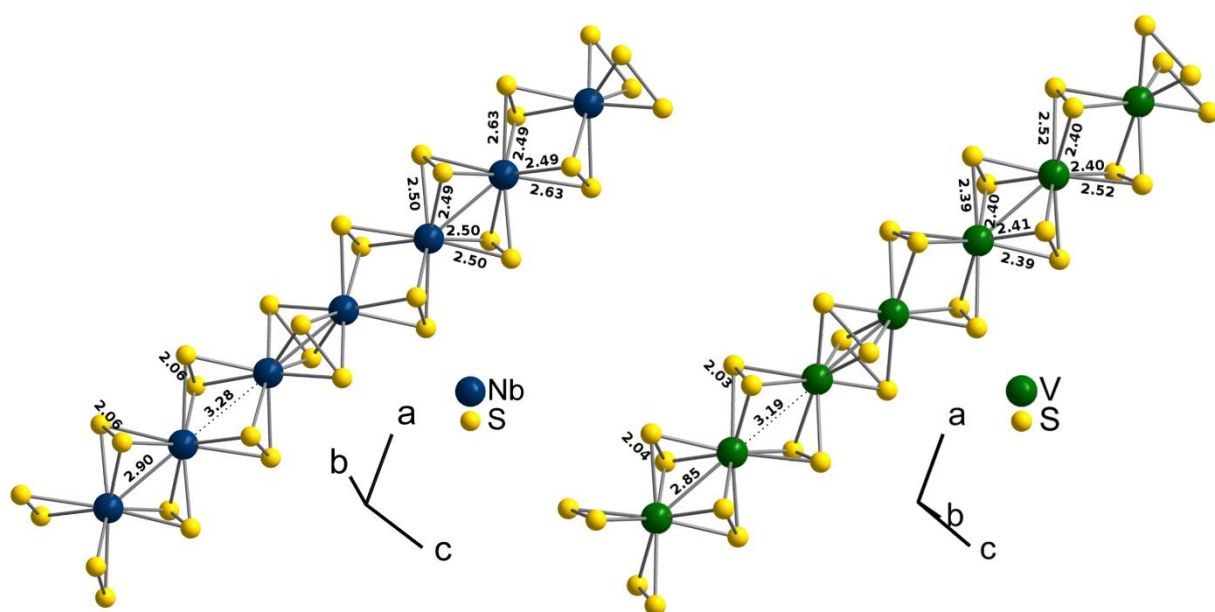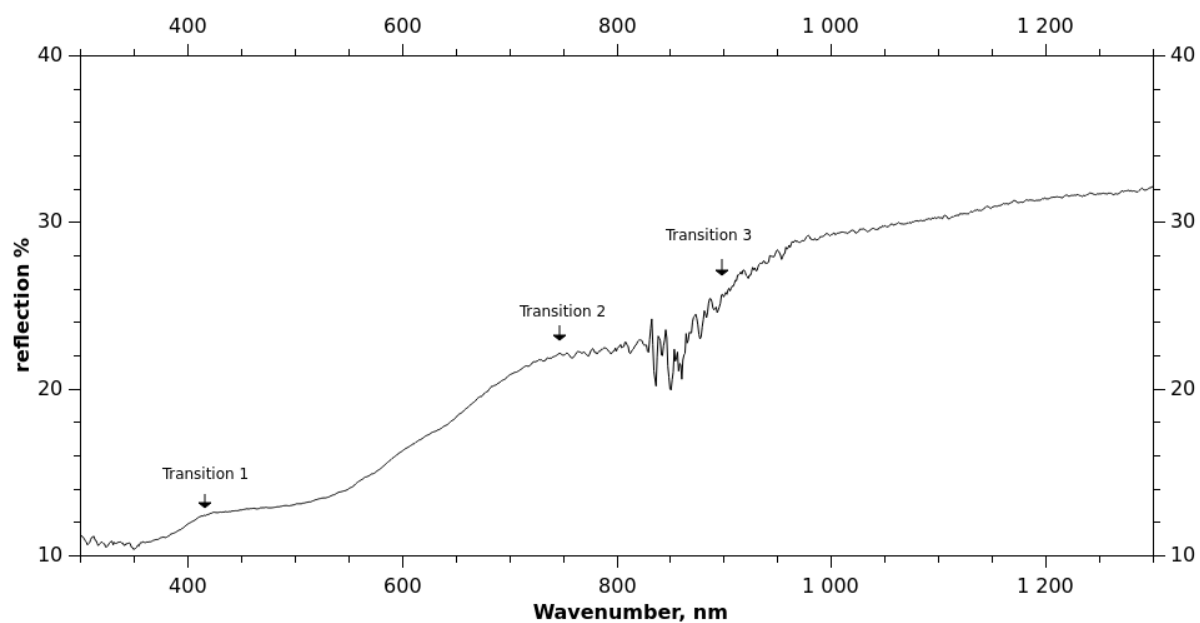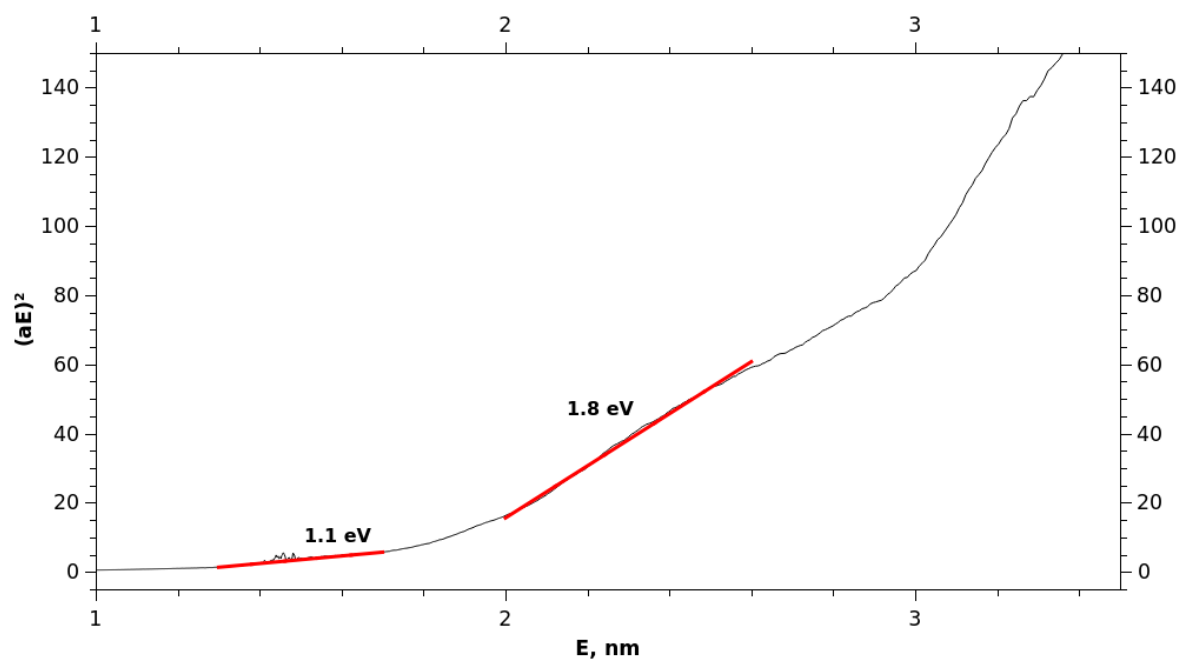|  | $c = 6.9509(11)$ Å, $\beta = 111.939(5)°$ | $c = 6.951$ Å, $\beta = 110.87°$ | $c = 6.7494(4)$ Å, $\beta = 110.825(1)°$ |
|---|---|---|---|
| Distances |  |  |  |
| M–M, Å | 2.896 3.278 | 2.954 3.38 | 2.853 3.192 |
| M–S, Å | 2.493-2.628 | 2.555-2.592 |  |
| S–S, Å | 2.060 2.065 | 2.145 2.159 | 2.027 2.039 |



Figure S5. Infinite chains in $NbS_4$ and $VS_4$ for comparison.

**a)**



**b)**

Figure S6.   Diffuse reflection spectrum (a) and Tauc plot (b) basing on the diffuse reflection spectrum of $NbS_4$ which was obtained from $Nb_{1.14}S_2$ (see the following graphic). From the latter plot, we see two band gaps which are estimated as 1.8 and 1.1 eV. The estimated value 1.1 eV is consistent with the calculated fundamental band gap, 1.07 eV.