

Electronic supplementary information

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Theoretical and experimental comparative study of stabilities and phase transformations of sesquichalcogenides M_2Q_3 ($M = Nb, Mo$; $Q = S, Se$)

Mariia N. Ivanova,^{a*} Andrey N. Enyashin,^b Ekaterina D. Grayfer,^a Vladimir E. Fedorov^{a, c*}

^a*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev prospect, Novosibirsk, 630090, Russian Federation*

^b*Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences, 91, Pervomayskaya st., Ekaterinburg, 620990, Russian Federation*

^c*Novosibirsk State University, 2, Pirogova st., Novosibirsk, 630090, Russian Federation*

E-mail: fed@niic.nsc.ru, kozlova@niic.nsc.ru

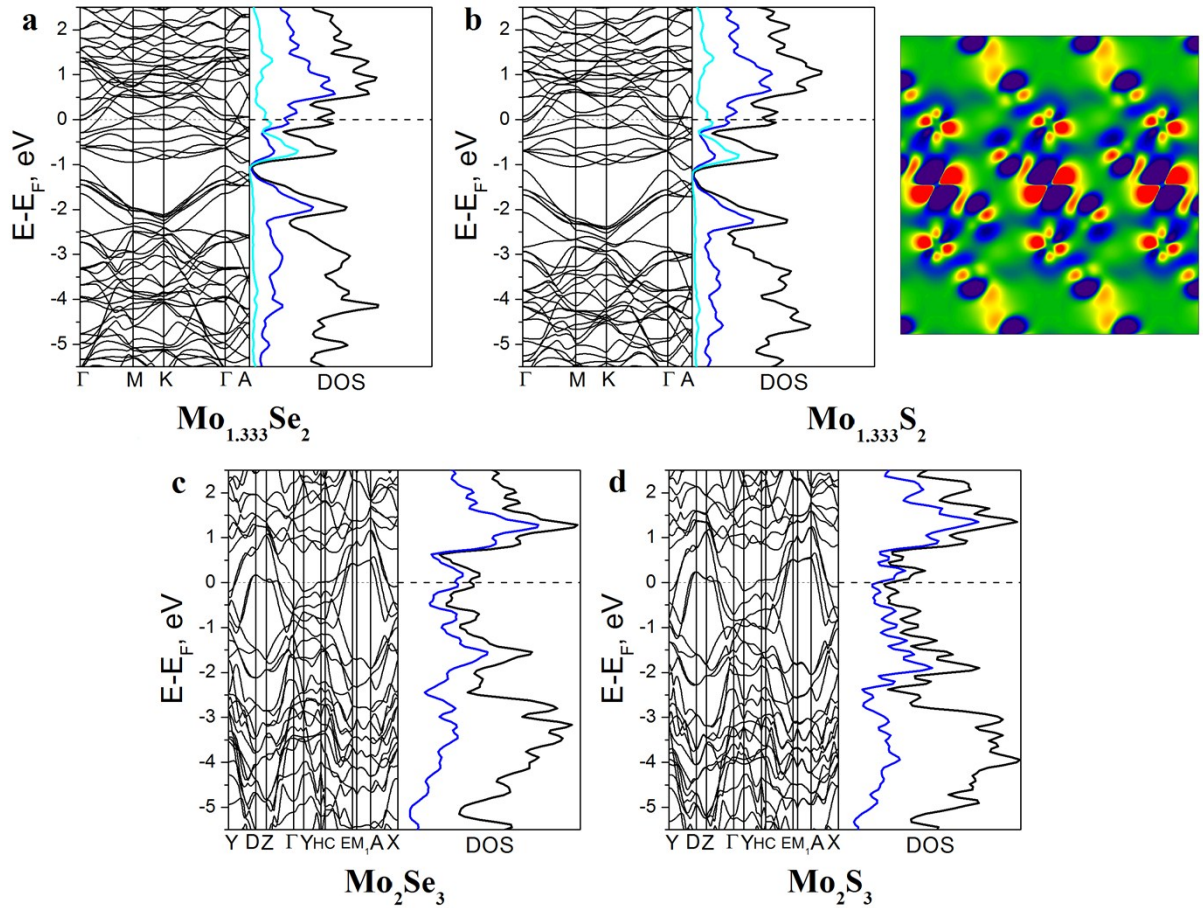


Fig. S1. Electronic band structure, total and partial Mo4*d* DOS for several molybdenum chalcogenides of stoichiometry Mo:Q = 2:3: **(a)** hypothetical intercalate $\text{Mo}_{1.333}\text{Se}_2$; **(b)** hypothetical intercalate $\text{Mo}_{1.333}\text{S}_2$; charge density redistribution $\Delta\rho$ within (100) plane of $\text{Mo}_{1.333}\text{S}_2$ is mapped, depicting the charge transfer from the intercalating Mo atoms to the MoS_2 layers; **(c)** hypothetical sesquiselenide " Mo_2Se_3 "; **(d)** known sesquisulfide Mo_2S_3 . Total DOS is drawn as black line, while partial Mo4*d* DOS as blue or cyan lines for the atoms within layer or van der Waals gap, respectively. DFT GGA calculations.

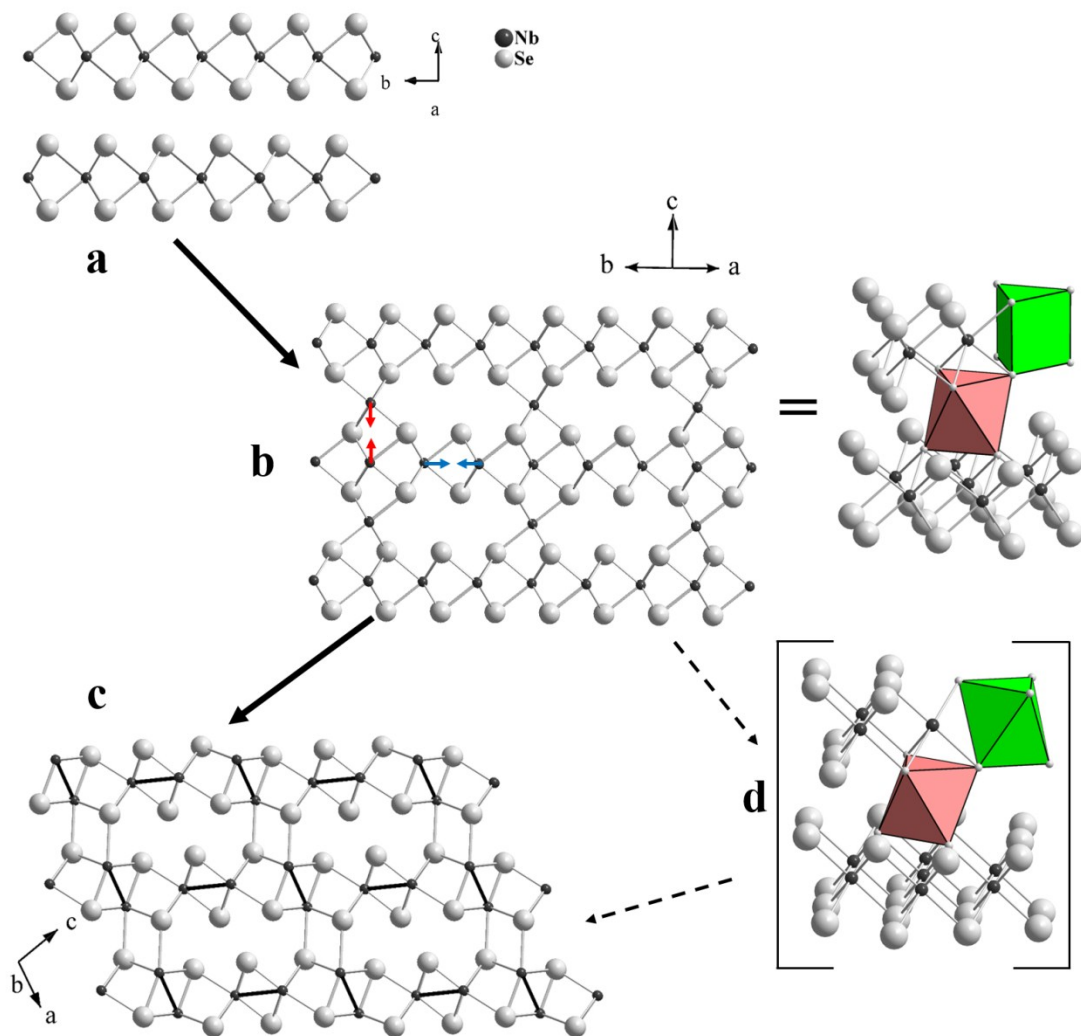


Fig. S2. Possible phase transformations in the Nb-Se system with stoichiometry 2:3: **(a)** First, NbSe₂ phase forms from the reaction of Nb and Se, and unreacted Nb exists as a second phase in the reaction mixture; **(b)** upon heating up to 500-600°C, Nb intercalation into the layered structure of NbSe₂ occurs, and the formation of the self-intercalated Nb_{1+x}Se₂ phase begins. The highest intercalation degree is achieved at $x = 0.33$ (2H-Nb_{1.33}Se₂, $P6_3/mmc$). “Interlayer” Nb atoms are spread statistically, and one of the possible options for the intercalated structure is shown here to illustrate conveniently how one structure may reorganize into the other. The right side of the image demonstrates coordination polyhedra of intercalated (pink) and intra-layer (green) Nb atoms; **(c)** at temperatures higher than 1000°C, polymorphic transformation to the iso-stoichiometric phase of Nb₂Se₃ ($P2_1/m$) occurs. It may be visualized by mentally moving the NbSe₂ layers and bringing every two Nb atoms closer to each other (red and blue arrows, **b**) to form two types of infinite covalent zigzag metal chains. The first type of chains forms when Nb atoms farthest from the intercalated ones “come closer” to each other (blue arrows in **b**). The second type of chains results from the “approaching” of the intercalated Nb atoms to the closest

ones within the NbSe_2 layers, so that the intercalated atoms “enter” the layer, and all the Nb atoms within chains become equivalent (red arrows in **b**); **(d)** possible intermediate $2\text{T-Nb}_{1.33}\text{Se}_2$. Note the difference of coordination polyhedra from **b** and **d**.

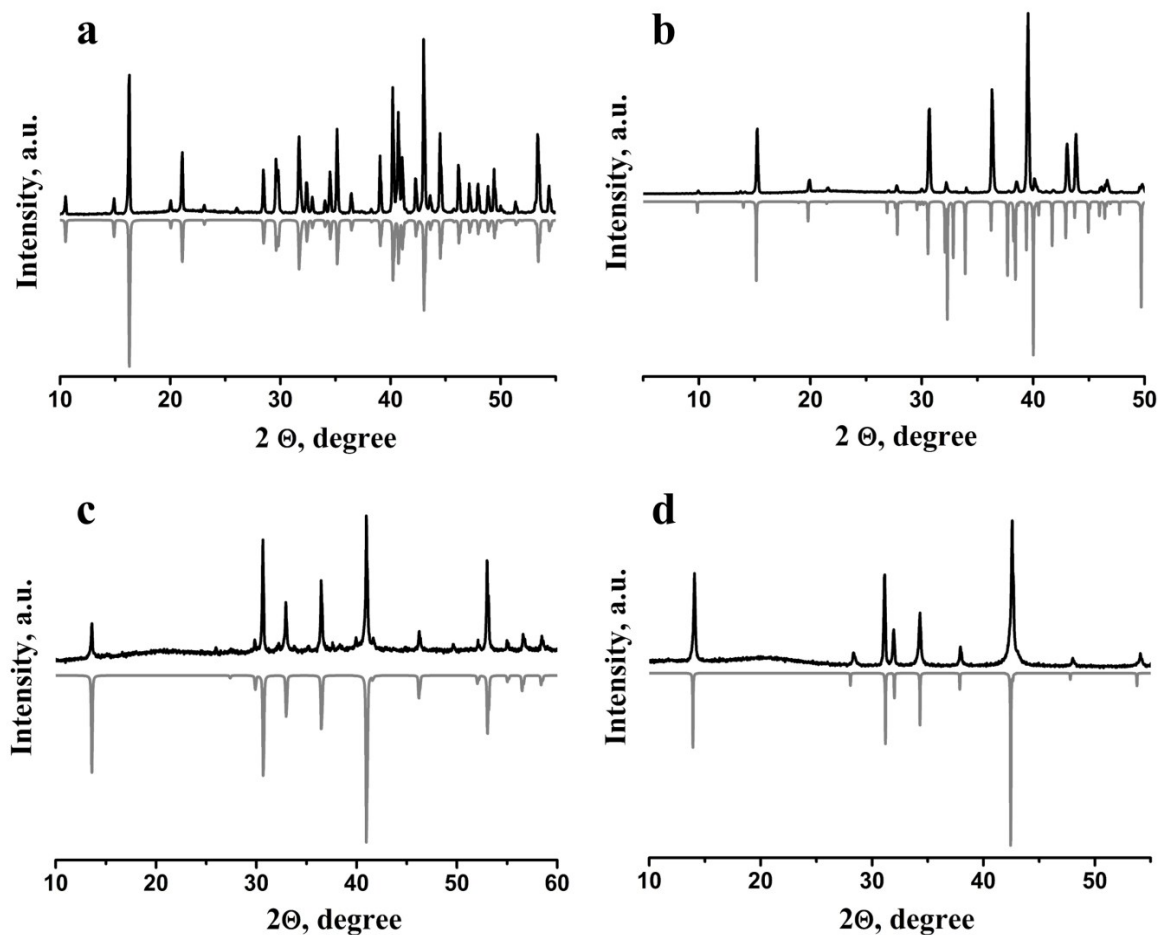


Fig. S3. XRD data for powdered samples (black lines) compared with theoretical diffraction patterns calculated from crystal data (gray lines): **(a)** Mo_2S_3 sample and pattern for PDF 01-081-2031; **(b)** Nb_2Se_3 sample and pattern for PDF 01-089-2335 21-601; **(c)** $\text{Nb}_{1.33}\text{Se}_2$ sample (intercalated phase) and pattern for PDF 65-4791; **(d)** $\text{Nb}_{1.33}\text{S}_2$ sample (intercalated phase) and pattern for PDF 89-3044.

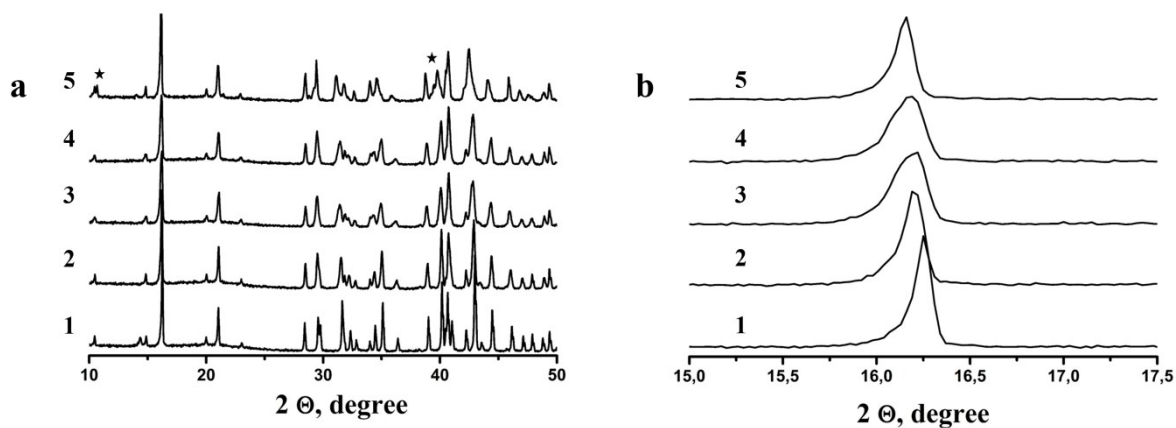


Fig. S4. XRD data for Mo₂S₃ sample (line 1) and a series of doped samples Mo_{2-x}Nb_xS₃ (x = 0.2; 0.3; 0.5 and 0.8, lines 2, 3, 4 and 5, correspondingly): **(a)** angle range from 10 to 50 degrees; black stars indicate impurity phase Nb₃S₄; **(b)** the enlarged angle range of (101) reflection.

Table S1. Lattice parameters, enthalpy (ΔH) and free energy at 1373 K (ΔG_{1373}) for the formation of various chalcogenide crystals with M:Q = 2:3 stoichiometry, according to DFT calculations. All energy values are tabulated relative to the data for sesquichalcogenides M_2Q_3 (M = Mo, Nb; Q = S, Se).

Compound	Sp. gr.	Z	Lattice parameters, Å or °	ΔH , eV/ M_2Q_3	ΔG_{1373} , eV/ M_2Q_3
1/3Mo+MoS ₂				-0.13	
Mo ₂ S ₃	<i>P</i> 12 ₁ / <i>m</i> 1	2	$a = 3.23$; $b = 6.22$; $c = 8.75$; $\alpha = 102.7$	0	
2H-Mo _{1.333} S ₂	<i>P</i> 6 ₃ 22	4	$a = 5.68$; $c = 12.36$	+0.63	+0.56
2T-Mo _{1.333} S ₂	<i>P</i> $\bar{3}$ 1 <i>c</i>	4	$a = 5.69$; $c = 12.43$	+0.85	+0.78
Nb ₂ Se ₃	<i>P</i> 12 ₁ / <i>m</i> 1	2	$a = 3.40$; $b = 6.48$; $c = 9.09$; $\alpha = 104.1$	0	
2H-Nb _{1.333} Se ₂	<i>P</i> 6 ₃ 22	4	$a = 5.94$; $c = 12.96$	+0.08	+0.01
2T-Nb _{1.333} Se ₂	<i>P</i> -31 <i>c</i>	4	$a = 5.98$; $c = 12.73$	+0.68	+0.61
2H-Nb _{1.333} S ₂	<i>P</i> 6 ₃ 22 (182)	4	$a = 5.68$; $c = 12.50$	-0.17	-0.24
Nb ₃ S ₄ + NbS ₂				-0.08	
Nb ₂ S ₃	<i>P</i> 12 ₁ / <i>m</i> 1 (11)	2	$a = 3.23$ Å; $b = 6.22$ Å; $c = 8.74$ Å; $\alpha = 102.7^\circ$	0	
NbS + NbS ₂				+0.39	
2T-Nb _{1.333} S ₂	<i>P</i> $\bar{3}$ 1 <i>c</i> (163)	4	$a = 5.76$; $c = 12.24$	+0.49	+0.42
Mo ₃ Se ₄ + MoSe ₂				-0.15	
Mo ₂ Se ₃	<i>P</i> 12 ₁ / <i>m</i> 1	2	$a = 3.33$; $b = 6.47$; $c = 9.12$; $\alpha = 103.0$	0	
2H-Mo _{1.333} Se ₂	<i>P</i> 6 ₃ 22	4	$a = 5.91$; $c = 12.82$	+0.66	+0.59
2T-Mo _{1.333} Se ₂	<i>P</i> 1 (1)	4	$a = 6.23$; $b = 6.23$; $c = 11.94$; $\alpha = 90.2$; $\beta = 89.9$; $\gamma = 59.5$	+0.66	+0.59