

SUPPORTING INFORMATION

Title:

**Extended chains in Vanadium O-centered complex $[V_4OSe_8I_5]_{\infty}$: synthesis,
structure and properties**

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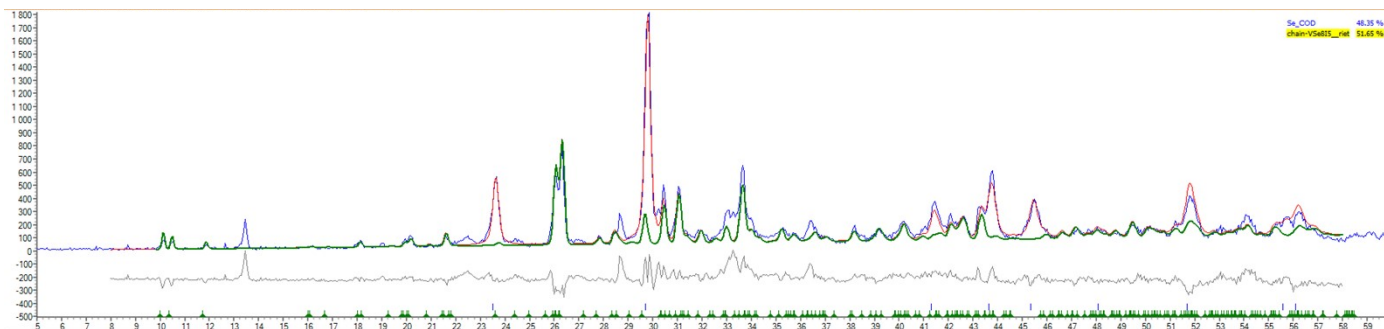


Figure S1. Initial view of adjustment of the experimental XRPD pattern of thermolysis products of $[\text{V}_4\text{OSe}_8\text{I}_6]\cdot\text{I}_2$ to a mixture of $[\text{V}_4\text{OSe}_8\text{I}_5]_\infty$ (**1**) and selenium, in Topas-Academic software. Blue line – experimental pattern, red line – selenium pattern, green line – $[\text{V}_4\text{OSe}_8\text{I}_5]_\infty$ pattern, grey line – difference between calculated and experimental pattern.



Figure S2. SEM picture of $[\text{V}_4\text{OSe}_8\text{I}_5]_\infty$ (**1**) crystals.

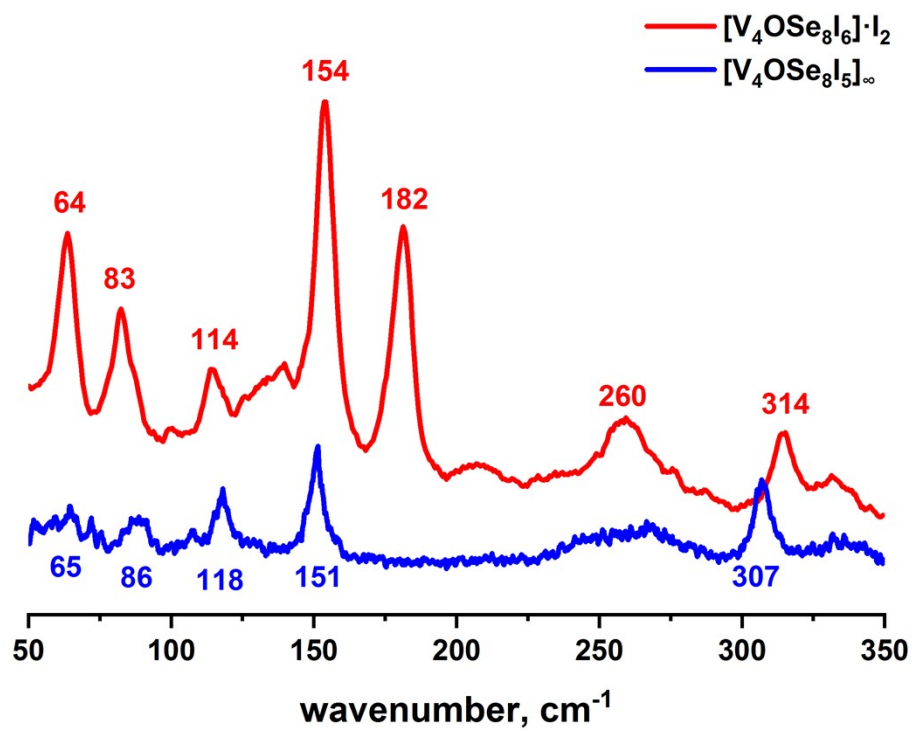


Figure S3. Comparison of Raman spectra of **1** and molecular compound $[V_4OSe_8I_6] \cdot I_2$.

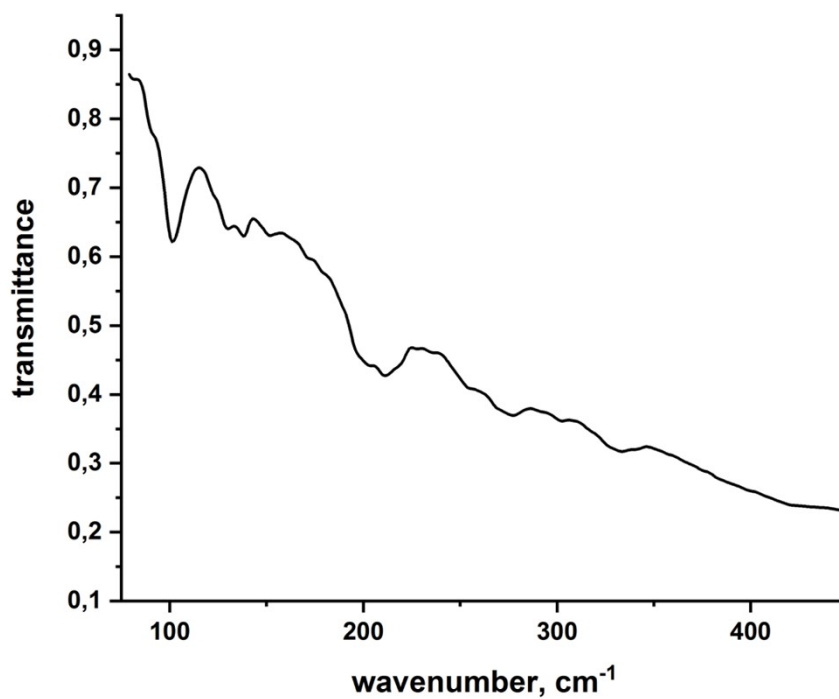


Figure S4. IR spectrum of **1** (far IR region)

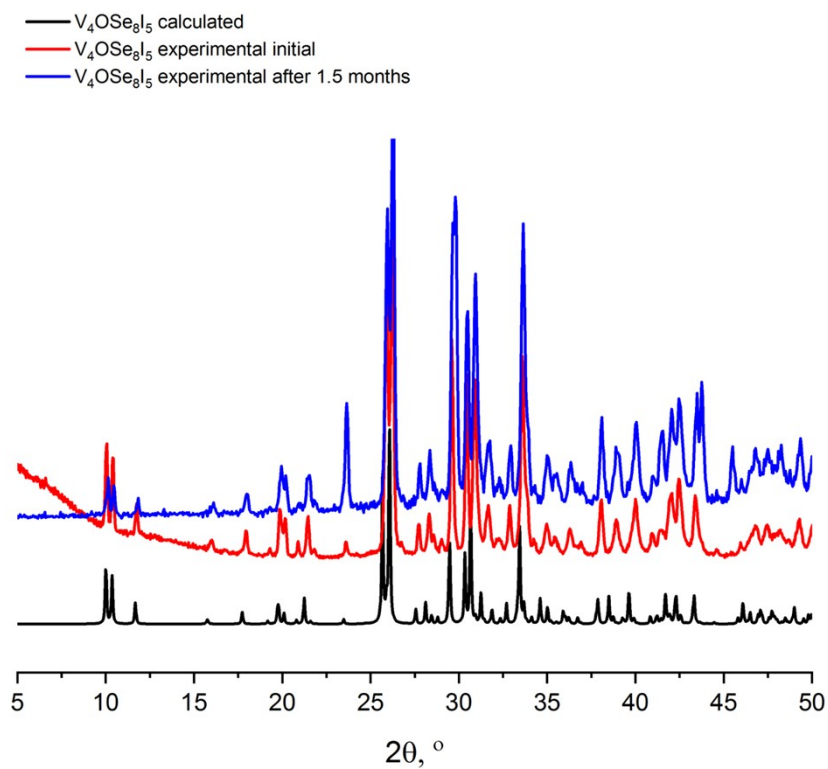


Figure S5. Powder diffraction patterns of the crystalline $V_4OSe_8I_5$ (**1**) performed with an interval of 1.5 months: red (initial) and blue (after 1.5 month storage) lines; black line - theory calculated powder pattern for **1**.

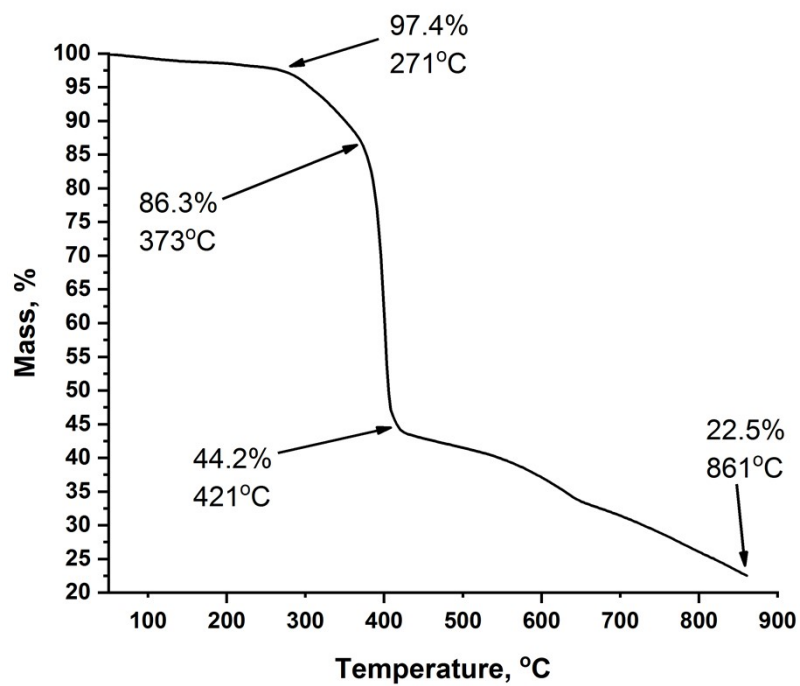


Figure S6. TG-curve of **1**

Table S7. Results of DFT-calculations

Formula	Z	Raw enthalpy calculated, Ry	Enthalpy calculated, kJ/mol of f.u.
V	2	-423.9967603895	-
Se	32	-5950.74318173	-
I ₂	4	-2983.3853734932	-
O ₂	1	-81.9576310378	-
VSe ₂	1	-584.0900671384	-223.4005361
VI ₃	6	-7985.1803512058	-125.3185764
VO ₂	4	-1178.238784	-792.2051194
[V ₄ OSe ₈ I ₆]·I ₂	4	-21443.96867	-1244.913552
[V ₄ OSe ₈ I ₅] _∞	4	-16968.76916	-1205.068326

Table S8. Comparison of band positions in IR spectrum of **1** with calculated for [V₄OSe₈I₆].
Prevailing vibration mode is also named for each band

Band position in sample 1 , cm ⁻¹	Calculated band position for [V ₄ OSe ₈ I ₆], cm ⁻¹	Assignment of the vibration band
90	91	ρ_r (V-Se ₂)
101	101	ν (V-V), two modes of vibrations with different symmetry
129	127	ν (V-Se ₂) asymmetric
138	137	ν (V-Se ₂) symmetric
152	147 and 148	ν (V-Se), two types of vibrations with different symmetry
212	220 and 221	ν (V-V), two types of vibrations with different symmetry
235	233	ν (V-I _{term}), with a change of geometry of the V4 fragment
253	264	ρ_r (V-Se), two modes of vibrations with different symmetry
277	286	ν (V-I _{bridge})

333	339	v (Se-Se) and simultaneously v (V-Se), two types of vibrations at this frequency, involving different pairs of Se ₂
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X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopic analysis (XPS) was performed on a spectrometer FLEXPS (Specs, Germany) equipped with electron energy analyzer Phoibos 150 and DLD detector. The excitation of electrons was carried out with Mg K α radiation. The pass energy was 20 eV, and the vacuum in the system was $\sim 10^{-10}$ mbar. The binding energies (BE's) were corrected using the line C1s = 284.7 eV from hydrocarbon surface contaminants. The lines were decomposed into components using the CasaXPS program¹. The lines C1s, O1s, N1s were decomposed into symmetric components as a product of Gaussian and Lorentzian functions. The spectrum of vanadium V2p_{1/2, 3/2} is a spin-orbital doublet. In the process of fitting the X-ray photoelectron spectra, the value of the spin-orbit splitting was fixed at ~ 7.33 eV and the ratio of the line intensities in the doublet was 0.5. The V2p_{1/2, 3/2} components were modeled by symmetrical Gauss-Lorentzian lines and additional satellite lines from each component. The V(IV) component is broadened and has a complex shape due to the appearance of a multiplet structure and was modeled by asymmetric Lorentzian components. The V2p_{1/2} components are broadened compared to V2p_{3/2} due to the Coster-Kronig Auger process. During the fitting, satellite lines for the V2p_{1/2, 3/2} components were also added.

Discussion of XPS for 1.

XPS V2p is located in the energy range 510-540 eV, next to the O1s region in the region of 530-535 eV (Fig. S8). For metallic vanadium², the components with BE for the 2p_{3/2} band are 512.15 eV; higher energies are attributed to higher oxidation states (up to 517.20 eV for V⁵⁺ in V₂O₅).

From our previous work, we also know that the bands for the complex can be shifted relative to oxides and take this into account when processing the spectra. For the molecular V₄OSe₈I₆·dmp (dmp = 3,5-dimethylpyrazole)³ the bands at 516.67 and 515.39 were assigned to the oxidation states +5 and +4, respectively. Since vanadium is in the +4 oxidation state in molecular compounds, we assign just this oxidation state to the 515.39 band, which is the main one in the spectrum of V₄OSe₈I₆·dmp, despite the fact that for vanadium oxides this BE corresponds more to V⁺³. XPS V 2p_{3/2} deconvolution of sample **1** yields bands at 516.65,

515.13, and 513.52 eV, which we referred to in the V^{5+} , V^{4+} and V^{2+} , respectively. The area ratio of the bands with BE 515.13 and 513.52 is close to 3 (2.92).

XPS O 1s: 530.37, 531.81, 533.45 eV. The presence of V^{5+} can be correlated with the impurity of surface vanadium oxide V_2O_5 , which is formed during storage of the substance; its approximate content is 8.7%. We assume that the main oxidation state of vanadium in **1** will be +4, as we observed for molecular compounds, with an admixture of +3, so that the total oxidation state is +3.75. However, in this case, the +2 component is present at 513.52 eV, and the area of this band exceeds that of the +4 component (V^{4+} - 23.3%, V^{2+} - 68.0%), while the corresponding V^{3+} band is absent at all. Based on the obtained BEs in the V2p spectrum, we tend to conclude that during the recording of the XPS spectra, partial reduction of vanadium occurs, and therefore the experimental spectrum only partially relates to compound **1**.

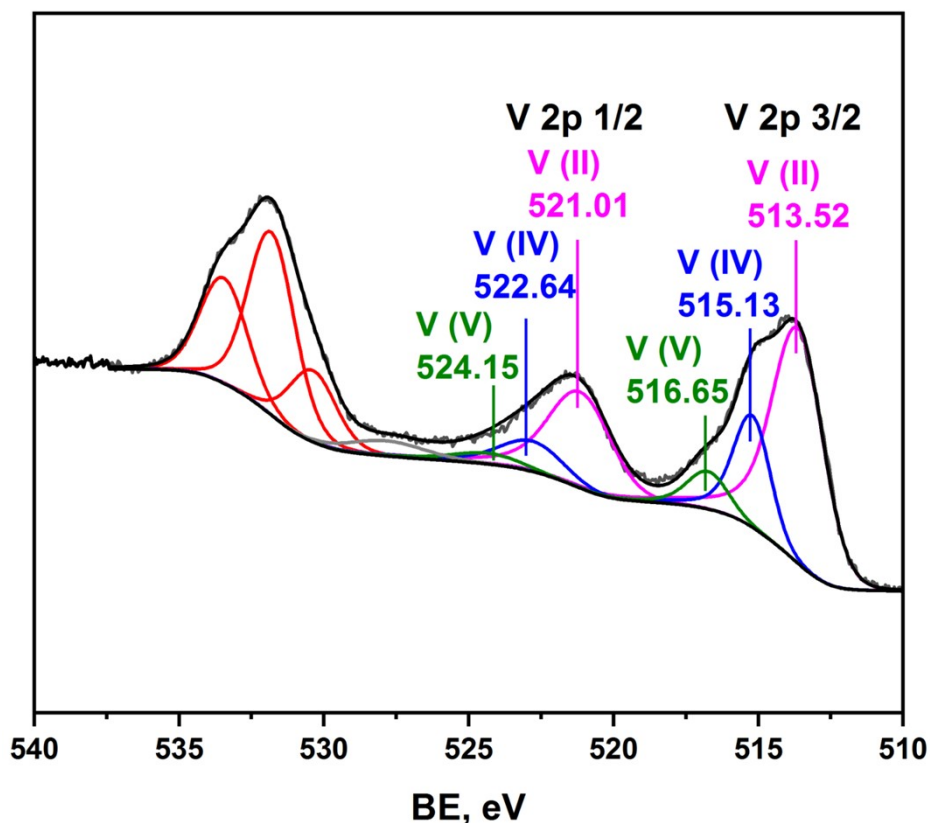


Figure S9. XPS O1s and V 2p of **1**

The characteristic range for Se is 52 - 58 eV (Fig. S9). The components BE 54.41 (Se 3d5/2) and 55.27 (Se 3d3/2) eV, according to the literature data on the previously described chalcogenide $(NbSe_4)_3I$ ⁴, in the structure of which only diselenide groups are present, can be attributed to Se_2^{2-} . These components are predominant in the spectrum of Se 3d. There is also

a small fraction of components 55.22 (Se 3d_{5/2}) and 56.08 eV (Se 3d_{3/2}), which can be assigned to elemental Se⁵.

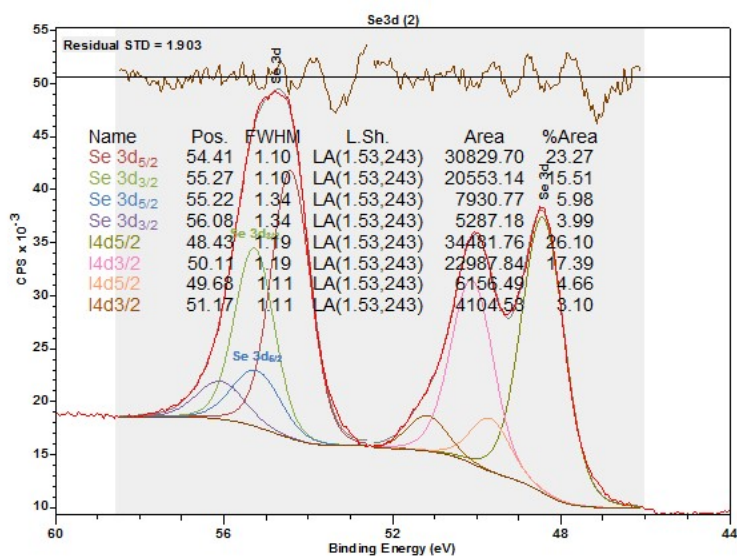


Figure S10. XPS Se3d spectrum of **1**

Bands with BE 615-634 eV correspond to I 3d (Fig. S10). Components 618.48 (I 3d_{5/2}) and 629.98 (I 3d_{3/2}) belong to I⁶ and make the main contribution to the corresponding peaks. The minor components 619.62 (I 3d_{5/2}) and 631.12 eV (I 3d_{3/2}) refer to I₂⁷.

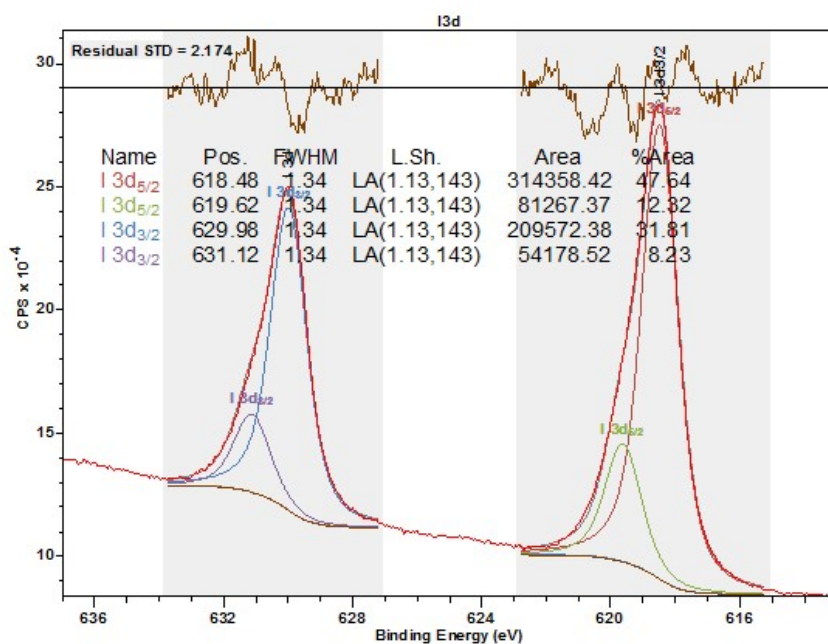
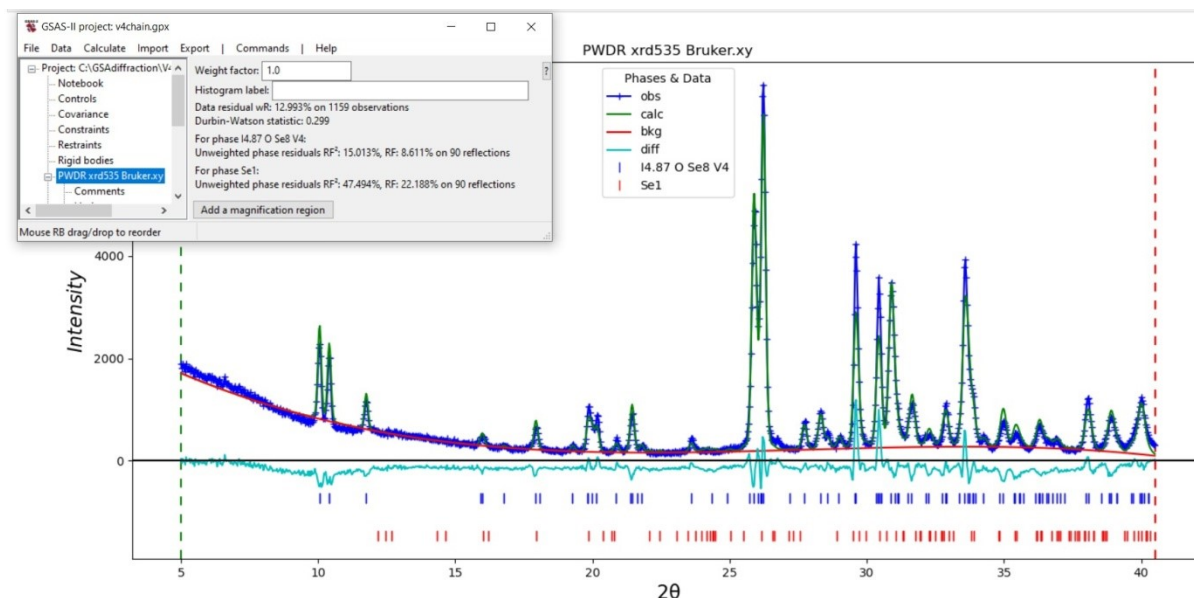


Figure S11. XPS I3d spectrum of **1**.Figure S12. Results of Rietveld refinement for bulk sample **1** used for resistivity measurements

References

- 1 N. Fairley, V. Fernandez, M. Richard-Plouet, C. Guillot-Deudon, J. Walton, E. Smith, D. Flahaut, M. Greiner, M. Biesinger and S. Tougaard, *Appl. Surf. Sci. Adv.*, 2021, **5**, 100112.
- 2 E. Hryha, E. Rutqvist and L. Nyborg, *Surf. interface Anal.*, 2012, **44**, 1022–1025.
- 3 R. R. Galiev, V. Y. Komarov, R. M. Khisamov, A. Y. Ledneva, S. B. Artemkina and V. E. Fedorov, *Inorganica Chim. Acta*, 2023, **548**, 121366.
- 4 P. Gressier, A. Meerschaut, L. Guemas, J. Rouxel and P. Monceau, *J. Solid State Chem.*, 1984, **51**, 141–151.
- 5 B. Canava, J. Vigneron, A. Etcheberry, J. F. Guillemoles and D. Lincot, *Appl. Surf. Sci.*, 2002, **202**, 8–14.
- 6 Z. Bastl and H. Gehlmann, *Collect. Czechoslov. Chem. Commun.*, 1988, **53**, 425–432.
- 7 G. Kalita, K. Wakita, M. Takahashi and M. Umeno, *J. Mater. Chem.*, 2011, **21**, 15209–15213.