Supplementary information

Further data involving 1:2 and 1:3 ratio mixtures.

The view presented above is coherent for explaining the behaviour observed in the figures S1 (a) and (b) respectively after extended ball milling and thermal treatments:

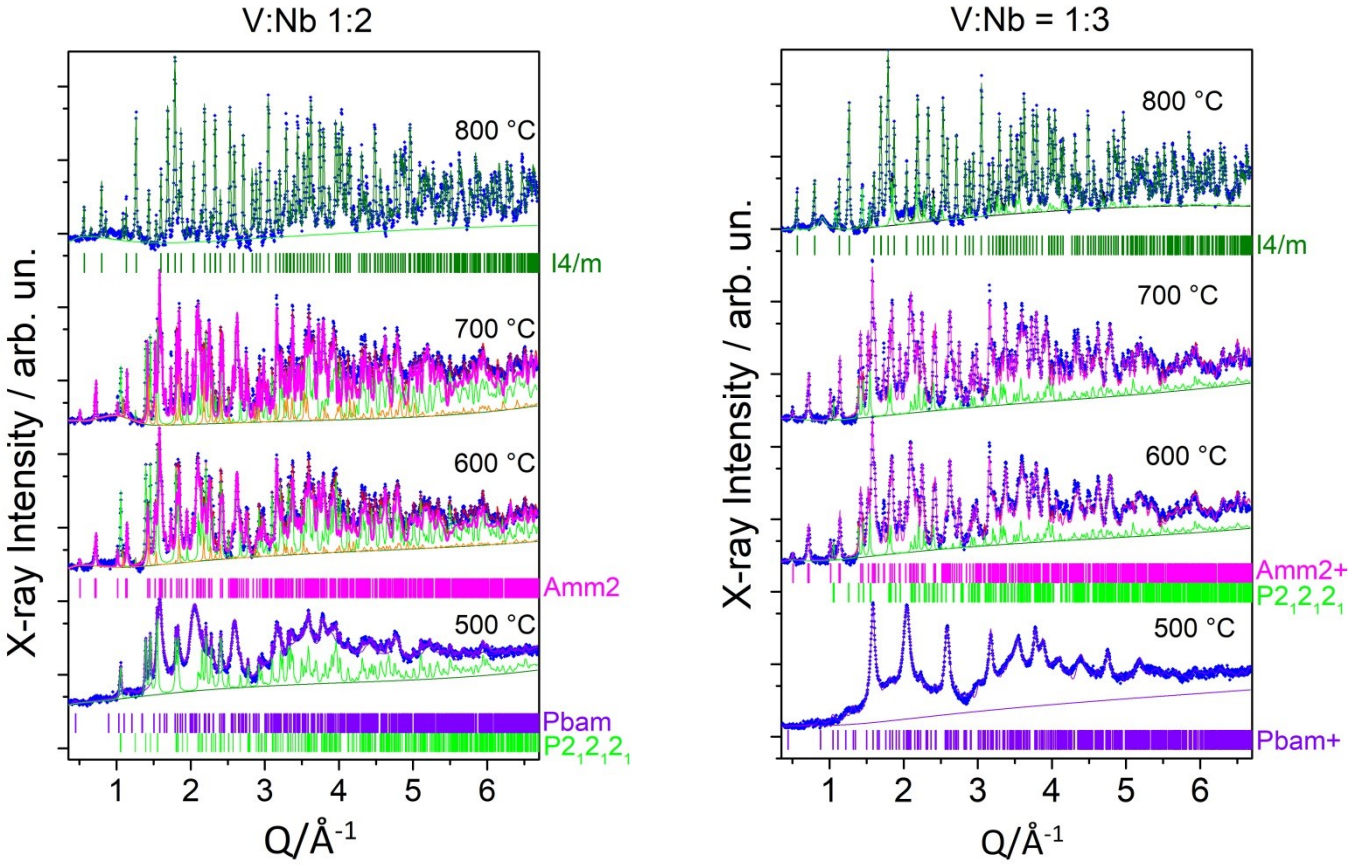

Figure S1

The XRD patterns (laboratory equipment) of the 1-to-2 and 1-to-3 V_2O_5-Nb_2O_5 molar mixtures ball milled for 24 h and subjected to ex-situ thermal annealing (holding time 2 h) at the indicated temperatures.

We can see that for the 1:2 mixture ratio, the XRD ex-situ experiment after annealing at 500 °C displays occurrence of the pseudo-hexagonal sequence (presumably a solid solution with composition $[V_{0.33}Nb_{0.67}]_2O_5$ described with a distorted *Pbam* space group) and the equimolar $P2_12_12_1$ compound[1] (originally attributed to the *Pnma* space group[2]). After further annealing at 600 °C and

700 °C respectively, we observe the occurrence of the orthorhombic *Amm2* VNb_5O_{15} phase with the $P2_12_12_1$ $VNbO_5$ phase. Note that the cyan line component used to represent the $VNbO_5$ phase is weakened going from 600 °C to 700 °C. Finally, after annealing at 800 °C (holding time 2 h) the total occurrence of the VNb_9O_{25} phase is confirmed, which supports the view of V_2O_5 evolution operating beyond the specific transformation processes.

The 1:3 mixture shows a similar behavior at the parity of annealing treatments (*Figure S1*). Here the amorphous component seems to have resisted to the temperature treatment at 500 °C at least partially. For the temperature treatments of 600 °C and 700 °C, respectively, we observe again the simultaneous occurrence of the *Amm2* VNb_5O_{15} phase together with the $P2_12_12_1$ $VNbO_5$ phase, the latter in a lower quantity concerning the corresponding patterns shown in the lhs figure, in rough agreement with the expectation from the lever rule. Weak traces of V_2O_5 phase are also appreciable at 800°C suggesting a disproportionation of metastable phases (*Amm2* and $P2_12_12_1$) eventually evolving to VNb_9O_{25} and V_2O_5, regardless of the starting reagents ratio.

TEM analysis

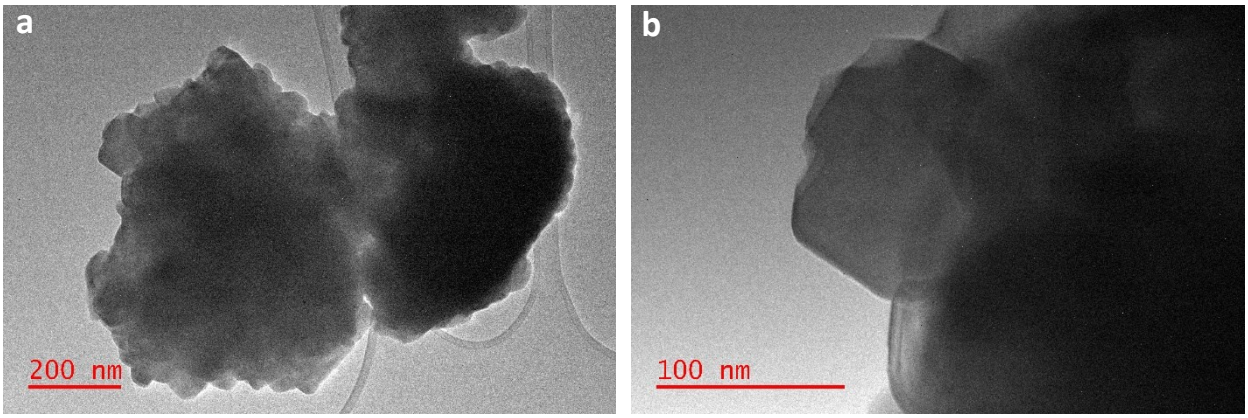

Figure S2

TEM micrographs of the sample annealed at 700° C at different magnifications.

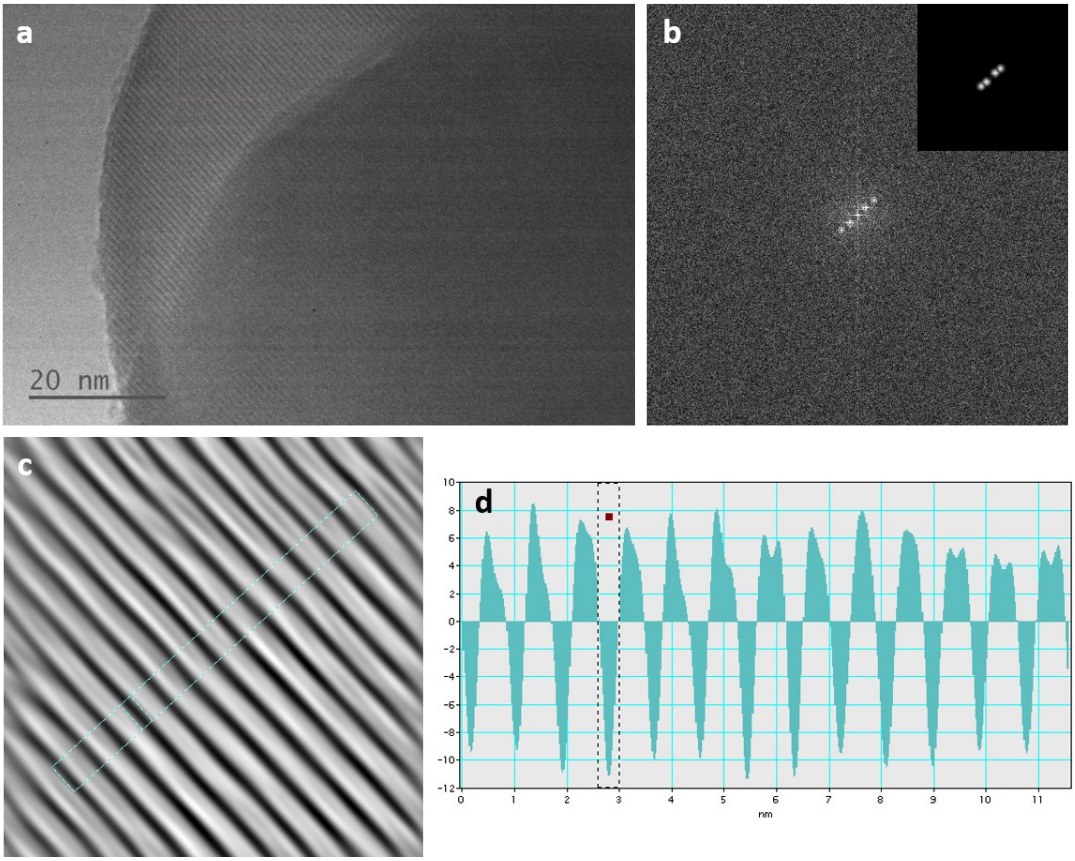

Figure S3.

a) HR-TEM image, b) FFT applied to the oriented crystalline planes and its residual masked contribution on the inset, c) inverse FFT and d) integrated area.

TABLE S1

List of the nearest neighbours interatomic distances around V and Nb metal species, according to their location in Wyckoff sites.

V2-O1	1.590
-O1	1.590
-O16	1.818
-O10	2.012
-O10	2.012
V1-O16	1.634
-O2	1.986
-O2	1.986

-O17	2.112
-O17	2.113
Nb4-O3	1.793
-O17	2.135
-O8	2.152
-O8	2.152
Nb5-O17	1.869
-O7	1.872
-O11	2.001
-O11	2.001
Nb2-O4	1.820
-O3	1.857
-O14	2.030
-O14	2.030
-O6	2.163
Nb3-O6	1.931
-O12	1.985
-O12	1.986
-O1	2.065
-O1	2.065
Nb1-O15	1.996
-O9	2.032
-O9	2.032
-O1	2.208
-O5	2.230

Nb6-O7	1.843
-O7	1.843
-O18	1.991
-O18	1.991
-O4	2.141
-O4	2.141

References:

1 J. Hidde, C. Guguschev and D. Klimm, *J. Cryst. Growth*, 2019, **509**, 60–65.

2 J. M. Amarilla, B. Casal and E. Ruiz-Hitzky, *J. Mater. Chem.*, 1996, **6**, 1005–1011.

3 D. R. G. Mitchell, *Microsc. Res. Tech.*, 2008, **71**, 588–593.