## Oxygen diffusion in the orthorhombic FeNbO<sub>4</sub> material: A computational study

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Table S1 The lattice parameters and lattice energy of the nonstoichiometric m-FeNbO<sub>4</sub> and o-FeNbO<sub>4</sub> structures from DFT simulations.

	a (Å)	b (Å)	c (Å)	β (°)	Lattice energy (eV/f.u.)
m-FeNbO <sub>4</sub>	4.723	5.706	5.023	89.97	-48.435
o-FeNbO <sub>4</sub>	4.705	5.679	5.040	89.69	-48.552

Table S2 The zero-point energy ( $E_{zero}$ ), entropy contribution (TS), vibrational contribution ( $U_{vib}$ ), and the Helmholtz free energy (F) of the monoclinic FeNbO<sub>4</sub> (m-FNO) and orthorhombic FeNbO<sub>4</sub> (o-FNO) at different temperatures from GULP simulations.

	0 K		700 k		1600 K	
	m-FNO	o-FNO	m-FNO	o-FNO	m-FNO	o-FNO
Lattice energy (eV)	-482.8	-482.7	-482.8	-482.7	-482.8	-482.7
Ezero (eV)	0.786	0.785	0.78	0.78	0.78	0.78
TS (eV)	-	-	2.63	2.61	9.78	9.73
U <sub>vib</sub> (eV)	-	-	1.99	1.99	4.55	4.55
F (eV)	-482.0	-481.9	-483.4	-483.3	-488.0	-487.8



Figure S1 The 1×1×1 bulk structures obtained from experiments: (a) experiment 1; (b) experiment 2; (c) experiment 3; (d) experiment 4; red is oxygen, brown is Fe, and green is Nb.



Figure S2 The 2×2×2 bulk structures obtained from experiments: (a) experiment 1; (b) experiment 2; (c) experiment 3; (d) experiment 4; red is oxygen, brown is Fe, and green is Nb .



Figure S3 The magnetic structure used in this work; red is oxygen, brown is Fe, and green is Nb.



Figure S4 The stable interstitial site of the extra oxygen in the 2×2×2 supercell.



Figure S6 The diffusion pathway of the interstitial oxygen atom along the [010] direction (a) and the [100] direction (b) in the Int1 network of the ordered stoichiometric structure and their related variation of the total energy (c-d); red is oxygen, brown is Fe, and green is Nb and the yellow ball in (c,d) is the interstitial oxygen atom.



Figure S7 The diffusion pathway of the interstitial oxygen atom along the [010] direction (a) and the [100] direction (b) in the Int2 network of the ordered stoichiometric structure and their related variation of the total energy (c-d); red is oxygen, brown is Fe, and green is Nb and the yellow ball in (c,d) is the interstitial oxygen atom.