

## Isolating the two room-temperature polymorphs of $\text{NaNbO}_3$ : structural features, optical band gap and reactivity

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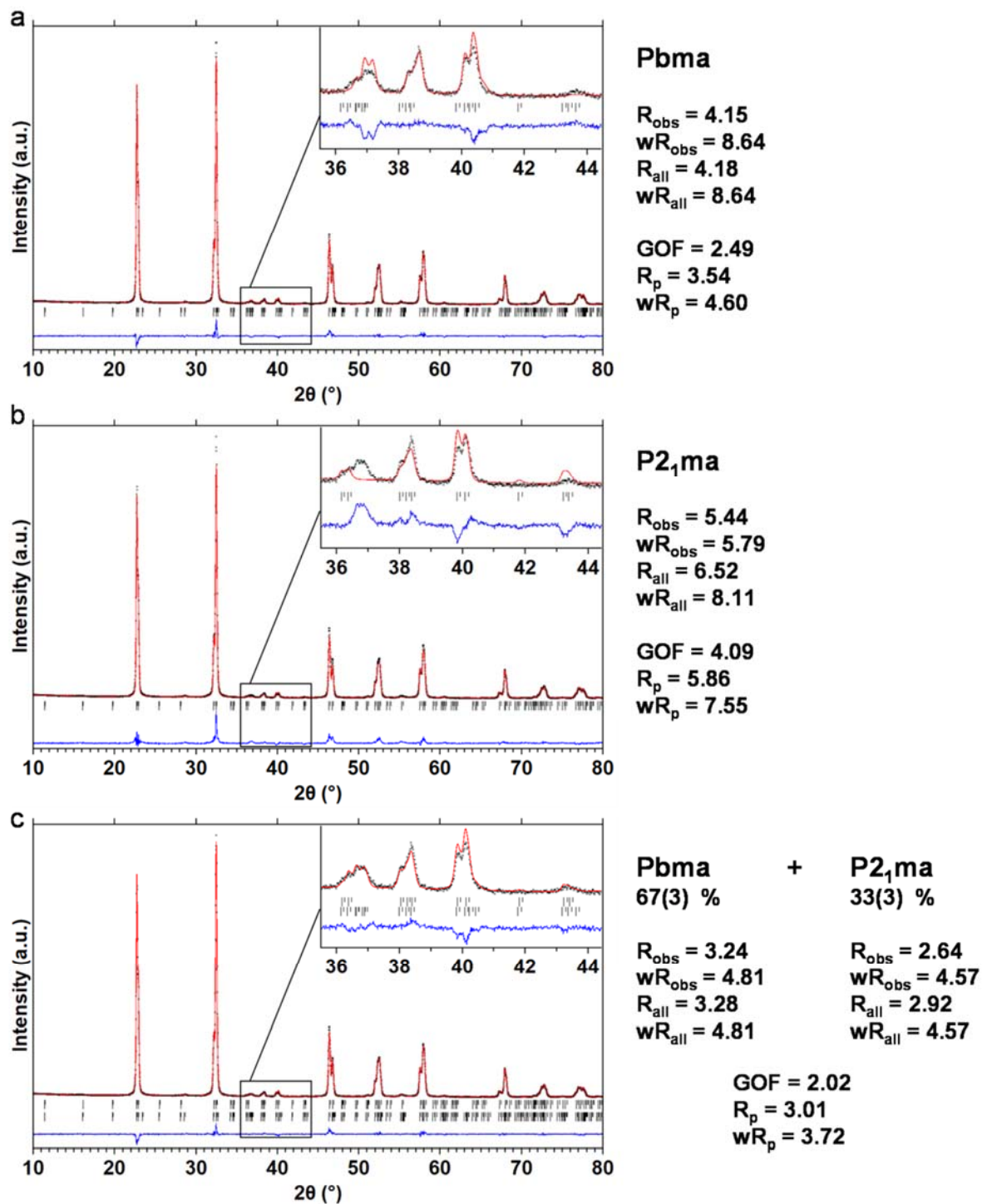
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**Figure S1.** Rietveld refinements of  $\text{NaNbO}_3$  powder obtained after hydrothermal synthesis (no annealing).

**Table S1.** Na-Oi distances in  $\text{NaNbO}_3$  structures in the  $\text{Pbma}$  and  $\text{P2}_1\text{ma}$  space groups.

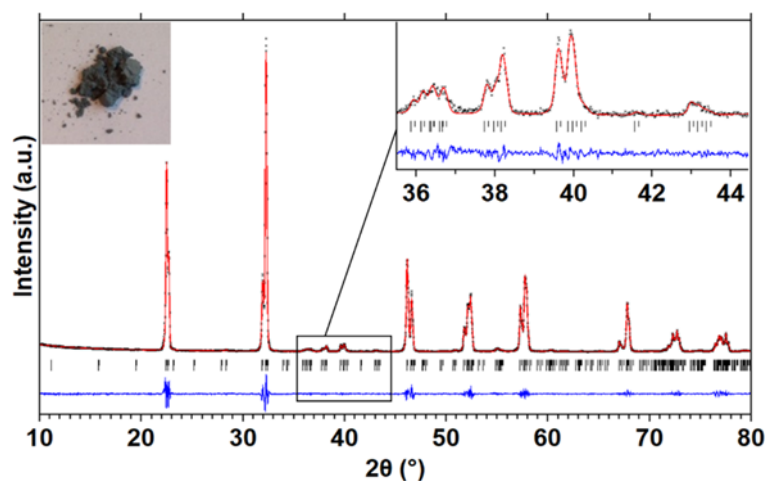
**Figure S2.** XRD pattern of  $\text{NaNbO}_{3-x}$  after exposure of  $\text{P2}_1\text{ma-NaNbO}_3$  to  $\text{Ar:H}_2$  (95:5 %vol.) at 1000 °C during 1 h, and refinement using profile matching method with  $\text{Pbma}$  structural hypothesis.



**Figure S1.** Rietveld refinements of  $\text{NaNbO}_3$  powder obtained after hydrothermal synthesis (no annealing), considering a) the Pbma space group, b) the  $\text{P2}_1\text{ma}$  space group and c) the two polymorphs in a phase mixture. In this last case, the refinement converges with a fraction of 67(3) % of the Pbma structure and 33(3) % of  $\text{P2}_1\text{ma}$  network. Rietveld refinements were performed with locked atomic positions of pure phases, that can be found in Table 1.

**Table S1.** Na-Oi distances in  $\text{NaNbO}_3$  structures in the  $\text{Pbma}$  and  $\text{P2}_1\text{ma}$  space groups. <sup>a</sup> Two oxygens at the same distance to the sodium site.

	d(Na1-Oi) (Å)		d(Na2-Oi) (Å)	
	Pbma	P2 <sub>1</sub> ma	Pbma	P2 <sub>1</sub> ma
avg	2.806	2.781	avg	2.746
O1	2.408(13)	2.526(3)	O2	2.414(14)
O1	2.794(1)	2.549(3)	O2	2.627(12)
O1	2.794(1)	3.009(3)	O2	3.021(12)
O1	3.097(13)	3.026(3)	O2	3.105(14)
O3 <sup>a</sup>	2.805(8)	2.734(2)	O3 <sup>a</sup>	2.418(9)
O3 <sup>a</sup>	3.144(8)	3.061(2)	O3 <sup>a</sup>	2.601(9)
O4 <sup>a</sup>	2.433(9)	2.465(2)	O4 <sup>a</sup>	2.627(9)
O4 <sup>a</sup>	2.910(9)	2.871(2)	O4 <sup>a</sup>	3.248(9)



**Figure S2.** XRD pattern of  $\text{NaNbO}_{3-x}$  after exposure of  $\text{P2}_1\text{ma-NaNbO}_3$  to  $\text{Ar:H}_2$  (95:5 %vol.) at  $1000\text{ }^\circ\text{C}$  during 1 h (black crosses), refinement using profile matching method with  $\text{Pbma}$  structural hypothesis (red curve) and difference between experiment and calculation (blue curve). The XRD powder sample was prepared in a nitrogen-filled glovebox and maintained in a sealed sample holder to prevent any oxidation. Kapton walls were positioned along the XRD beam path to ensure data collection. Relatively high reliability factors ( $\text{GOF} = 1.52$ ,  $\text{Rp} = 6.16\%$  and  $\text{wRp} = 8.59\%$ ) are attributed to a lower signal-to-noise ratio, due to acquisition with a sealed sample-holder mounted with Kapton walls.