## Polymorphism, structural characterisation and electrical properties of Na<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub>

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## **Electronic Supplementary Information**



**Fig S1.** Nb–O bond lengths *vs* temperature for NbO<sub>6</sub> octahedra. Error bars represent  $2\sigma$ . Atoms in *R*–3*c* split in *C*2/*c* as follows: Na(1)  $\rightarrow$  Na(1), Nb(1)  $\rightarrow$  Nb(1,2), Nb(2)  $\rightarrow$  Nb(3), O(1)  $\rightarrow$  O(1,2,3), O(2)  $\rightarrow$  O(4,6) and O(3)  $\rightarrow$  O(5).



**Fig S2.** Na–O bond lengths *vs* temperature for NaO<sub>7</sub> polyhedra. Error bars represent  $2\sigma$ . Atoms in *R*–3*c* split in *C*2/*c* as follows: Na(1)  $\rightarrow$  Na(1), Nb(1)  $\rightarrow$  Nb(1,2), Nb(2)  $\rightarrow$  Nb(3), O(1)  $\rightarrow$  O(1,2,3), O(2)  $\rightarrow$  O(4,6) and O(3)  $\rightarrow$  O(5).



**Fig S3.** Nb–O bond lengths *vs* temperature for NbO<sub>7</sub> pentagonal bipyramids. Error bars represent  $2\sigma$ . Atoms in *R*–3*c* split in *C*2/*c* as follows: Na(1)  $\rightarrow$  Na(1), Nb(1)  $\rightarrow$  Nb(1,2), Nb(2)  $\rightarrow$  Nb(3), O(1)  $\rightarrow$  O(1,2,3), O(2)  $\rightarrow$  O(4,6) and O(3)  $\rightarrow$  O(5).



Fig S3. Continued.