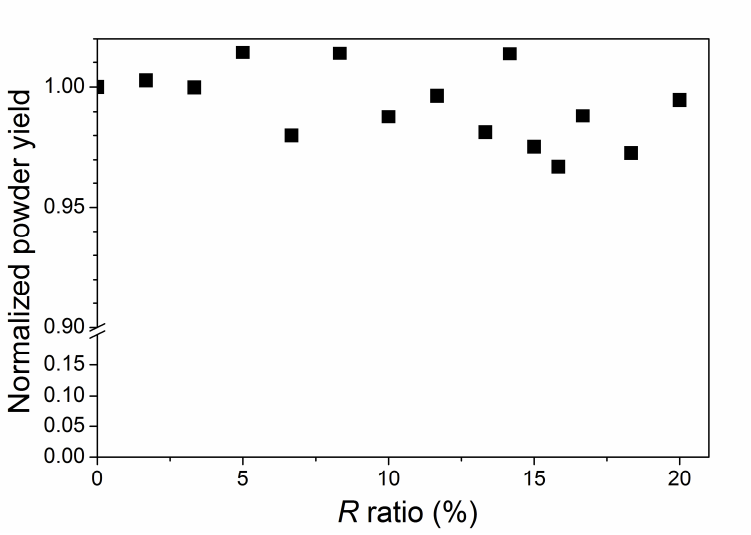
SUPPORTING MATERIALS AVAILABLE

1. **Normalized powder yield of as synthesized NKN**



Supporting Figure 1: Normalized powder yield of as synthesized NKN powder. Normalization processes take into account the sodium atom occupancy, $NaNbO_3$ second phase and theoretical yield for $KNbO_3$ and $NaNbO_3$

2. TOPAS® refinement codes used in this study

Two separate refinement codes were used; those of phase "M" are shown in Supporting Table 1 with starting values taken from $KNbO_3$ CIF file. Sodium atoms were assumed to occupy a fraction of K sites, and total occupancy was assumed full. Similar treatment was applied to niobium and oxygen atom sites. To improve background fitting, two broad peak phases near 10° and 15° 2θ were inserted in addition to the usual fourth order Chebychev background fitting function. These broad peaks represent known incoming source and background peak from the Philips MPD X'Pert XRD machine and always appear regardless the type of the samples mounted.

Supporting Table 1: Refinement codes for A*mm2* spacegroup

Site	Np	x	y	z	Atom	Occ.	Beq.
Nb1	4	@	=0	=0	Nb+5	Fix	!BNb
K1	2	=1/2	=0	@	K+1	occ	!BK
					Na+1	=(1-occ)	=BK
O1	2	=1/2	=0	@	O-2	Fix	!BO
O2	4	=0	@	@	O-2	Fix	=BO

For "L" phase samples, different refinement codes were used (Supporting Table 2) because of the reduced symmetry. In addition to basic starting value and occupancy consideration taken in "M" phase, additional constraints assuming ideal perovskite were used: (1) For Oxygen atoms, the regular octahedra were assumed to tilt as rigid units[60]. (2) Two independent Niobium atoms were put equal and the displacements were required to be strictly two-corner. (3) For Sodium or Potassium atoms, restrictions caused by the regular Oxygen octahedral environments were taken into account. These constraints were achieved by tying the atomic movement of individual atoms to form "group" movement. For example in

oxygen atoms, although P*1m1* space group has sixteen distinct oxygen positions, most of them were tied together such that for entire oxygen positions in unit cells there were only three individually refined parameters.

Supporting Table 2: Refinement codes for P*1m1*.

Site	Np	x	y	z	Atom	Occ.	Beq.
Na1	1	xk1	=0	zk1	Na+1	a	!Na
					K+1	=1-a	=Na
Na2	1	=1/2-zk1	=0	=1-xk1	Na+1	=a	=Na
					K+1	=1-a	=Na
Na3	1	=xk1	=1/2	=zk1	Na+1	=a	=Na
					K+1	=1-a	=Na
Na4	1	=xk1	=1/2	=1-xk1	Na+1	=a	=Na
					K+1	=1-a	=Na
Na5	1	=1/2+xk1	=0	=1/2+zk1	Na+1	=a	=Na
					K+1	=1-a	=Na
Na6	1	=1-zk1	=0	=1/2-xk1	Na+1	=a	=Na
					K+1	=1-a	=Na
Na7	1	=1/2+xk1	=1/2	=1/2+zk1	Na+1	=a	=Na
					K+1	=1-a	=Na
Na8	1	=1/2+xk1	=1/2	=1/2-xk1	Na+1	=a	=Na
					K+1	=1-a	=Na
Nb1	2	xn1	yn1	=-xn1	Nb+5	Fix	!Nb
Nb2	2	=xn1	=yn1	=1/2-xn1	Nb+5	Fix	=Nb
Nb3	2	=1/2+xn1	=yn1	=1/2-xn1	Nb+5	Fix	=Nb
Nb4	2	=1/2+xn1	=yn1	=1-xn1	Nb+5	Fix	=Nb
O1	1	x1	=0	zo1	O-2	Fix	!o
O2	1	=-x1	=0	=1/2-zo1	O-2	Fix	=o

O3	1	=-x1	=1/2	=-zo1	O-2	Fix	=o
O4	1	=x1	=1/2	=1/2+zo1	O-2	Fix	=o
O5	2	x2	=1/4+zo1	=1/4	O-2	Fix	=o
O6	2	=1/4	=1/4+zo1	=-x2	O-2	Fix	=o
O7	2	=-x2	=1/4-zo1	=3/4	O-2	Fix	=o
O8	2	=1/4	=1/4-x1	=1/2+x2	O-2	Fix	=o
O9	1	=1/2+x1	=0	=1/2+zo1	O-2	Fix	=o
O10	1	=1/2-x1	=0	=-zo1	O-2	Fix	=o
O11	1	=1/2-x1	=1/2	=1/2-zo1	O-2	Fix	=o
O12	1	=1/2+x1	=1/2	=1+zo1	O-2	Fix	=o
O13	2	=1/2+x2	=1/4+zo1	=3/4	O-2	Fix	=o
O14	2	=3/4	=1/4+x1	=1/2-x2	O-2	Fix	=o
O15	2	=1/2-x2	=1/4-zo1	=1/4	O-2	Fix	=o
O16	2	=3/4	=1/4-x1	=-x2	O-2	Fix	=o