Supporting information

Structural analyses of a K_2O-rich $KNbO_3$ melt and the mechanism of $KNbO_3$ crystal growth

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Table S1 Calculated optical modes of the orthorhombic $KNbO_3$ crystal and their frequencies.

No.	Mode	Frequency (cm^{-1})
1	B_2	71.1
2	B_1	183.2
3	A_1	184.7
4	B_2	189.1
5	A_1	225.6
6	B_1	234.2
7	B_1	253.5
8	A_1	269.9
9	A_2	281.5
10	B_2	507.4
11	B_1	539.8
12	A_1	589.0

The orthorhombic $KNbO_3$ crystal belongs to the space group ***A***mm2 with two formula units in the unit cell and one formula unit (5 atoms) in the primitive cell. The irreducible representation for its normal vibrational modes, analyzed by group theory, has been reported by A. M. Quittet *et al* (*Phys. Rev. B*, 1976, **14** 5068－5072.) and Z. X. Shen *et al* (*Phys. Rev. B*, 1995, **52**, 3976－3980.). At $\boldsymbol{q} = 0$, $\Gamma = 5A_1 + A_2 + 5B_1 + 4B_2$. With exception of the acoustic modes $A_1 + B_1 + B_2$, the remainders ($4A_1 + A_2 + 4B_1 + 3B_2$) are optical modes. All the optical modes are Raman-active.

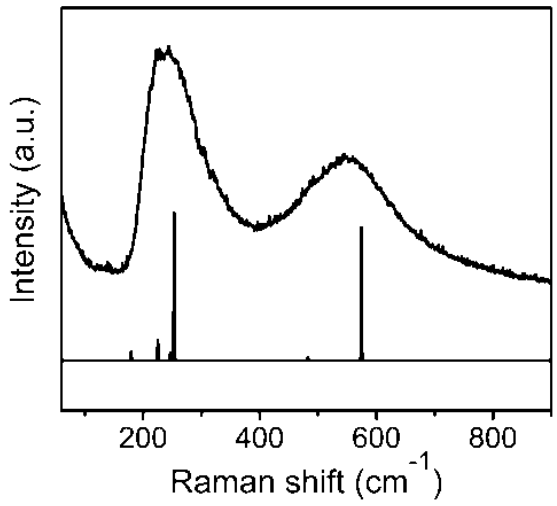


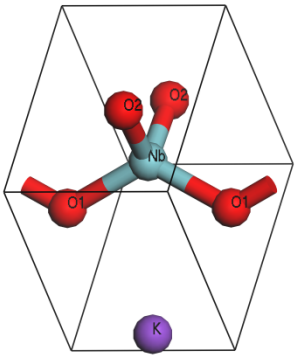
Fig. S1 Experimental (top) and calculated (bottom) Raman spectra of the tetragonal $KNbO_3$ crystal.

Table S2 Calculated optical modes of the tetragonal $KNbO_3$ crystal and their frequencies.

No.	Mode	Frequency (cm^{-1})
1	E	-132.5
2	A_1	179.2
3	E	180.3
4	B_2	225.2
5	E	246.6
6	A_1	253.2
7	E	482.6
8	A_1	574.4

The tetragonal $KNbO_3$ crystal belongs to the space group ***P*4*mm*** with one formula unit (5 atoms) in the unit cell. The irreducible representation for its normal vibrational modes, analyzed by group theory, is $4A_1 + 5E + B_2$ at $\boldsymbol{q} = 0$ (Γ point). With exception of the acoustic modes $A_1 + E$, the remainders ($3A_1 + 4E + B_2$) are optical modes. All the optical modes are Raman-active.

The cubic $KNbO_3$ crystal belongs to the space group ***Pm*3*m*** with one formula unit (5 atoms) in the unit cell. The irreducible representation for its normal vibrational modes, analyzed by group theory, is $4F_{1u} + F_{2u}$ at $\boldsymbol{q} = 0$ (Γ point). With exception of the acoustic modes F_{1u}, the remainders ($3F_{1u} + F_{2u}$) are optical modes. None of them are Raman-active. However, the cubic $KNbO_3$ crystal has two broad and intensive Raman bands in the experimental Raman spectra. The phenomenon can be explained on the basis of an order-disorder model of the central Nb ion (J. A. Baier-Saip, et al. *Solid State Commun.*, 2005, **135**, 367—372.).



Bond length (Å)	
Nb−O(1)	1.988
Nb−O(2)	1.799
K−O(1)	3.096
Bond angle (degree)	
O(1)−Nb−O(1)	123.50
O(2)−Nb−O(2)	102.23
O(1)−Nb−O(2)	107.29
O(1)−K−O(1)	68.90

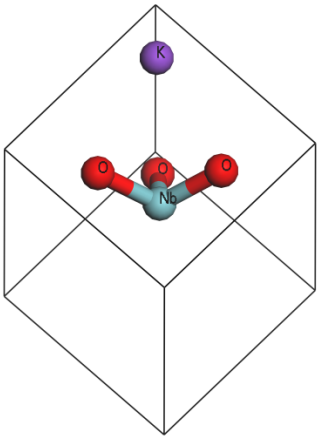
Fig. S2 Optimized structure of the K[$NbO_2Ø_2$] group. Crystal system: monoclinic; Space group: *P*1*m*1 (no. 6); Unit cell dimensions: $a = c = 5.1723$ Å; $b = 3.5032$ Å; $\beta = 93.33°$.

The optimized Nb−O bond lengths and O−Nb−O angles coincide with the reported values. (**Ref. 1:** F. D. Hardcastle and I. E. Wachs, *Solid State Ionics*, 1991, **45**, 201−213; **Ref. 2:** V. K. Trunov, V. A. Efremov, Yu. A. Velikodnyi and I. M. Averina, *Kristallografiya*, 1981, **26**, 67−71; **Ref. 3:** W. I. F. David, *Mater. Res. Bull.* 1983, **18**, 749−756.)

Table S3 Calculated optical modes of the K[$NbO_2Ø_2$] group and their frequencies.

No.	Mode	Frequency (cm^{-1})
1	*A″*	-48.6
2	*A′*	129.0
3	*A″*	167.5
4	*A′*	168.2
5	*A′*	198.4
6	*A″*	227.6
7	*A′*	303.7
8	*A′*	338.9
9	*A′*	486.1
10	*A″*	529.7
11	*A′*	770.7
12	*A′*	842.3

The melt unit cell belongs to the monoclinic space group ***P***1*m*1; each unit cell contains 5 atoms. Therefore, the melt has 15 vibrational modes (5*A*" + 10*A′*). With exception of the three acoustic modes *A*" + 2*A′*, the rest modes (4*A*" + 8*A′*) are optical modes and all Raman-active.



Bond length (Å)	
Nb−O	1.800
K−O	3.132
Bond angle (degree)	
O−Nb−O	105.16
O−K−O	54.31

Fig. S3 Optimized structure of the K[NbO_3] group. Crystal system: trigonal; Space group: *R*3*m* (no. 160); Unit cell dimensions: $a = c = 5.3194$ Å.

The Nb−O bond lengths and O−Nb−O angles are close to the reported values. (**Ref. 1:** A. W. Hewat, *J. Phys. C*, 1973, **6**, 2559−2572; **Ref. 2:** P. Seidel and W. Hoffmann, Z. fuer Kristallogr. Kristallgeom. Kristallphys. Kristallchem., 1976, **143**, 444−459.)

Table S4 Calculated optical modes of the K[NbO_3] group and their frequencies.

No.	Mode	Frequency (cm^{-1})
1	A_2	43.0
2	E	101.0
3	E	101.0
4	A_1	116.6
5	E	164.2
6	E	164.2
7	A_1	291.9
8	E	310.9
9	E	310.9
10	E	782.7
11	E	782.7
12	A_1	889.5

The melt unit cell belongs to the monoclinic space group ***R***3*m*, containing 5 atoms. Therefore, the melt has 15 vibrational modes ($4A_1 + A_2 + 5E$). With exception of the three acoustic modes $A_1 + E$, the rest modes ($3A_1 + A_2 + 4E$) are optical modes, among which $3A_1 + 4E$ are Raman-active.