

Supplementary Information

Cation Induced Structural Variation in Topochemically Modified Dion-Jacobson Perovskite Solid Solutions

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Figures

X-ray diffraction data

Figure S1. X-ray diffraction data for $\text{ALa Nb}_2\text{O}_7$ for (a) $\text{LiLa Nb}_2\text{O}_7$, (b) $\text{NaLa Nb}_2\text{O}_7$, (c) $\text{KLa Nb}_2\text{O}_7$, (d) $\text{RbLa Nb}_2\text{O}_7$, and (e) $\text{CsLa Nb}_2\text{O}_7$.

Figure S2. X-ray diffraction data for parent compounds, $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li, Na, K, Rb, Cs}$).

Figure S3. X-ray diffraction data for $\text{Li}_{1-x}\text{Na}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Figure S4. X-ray diffraction data for $\text{Na}_{1-x}\text{K}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Figure S5. X-ray diffraction data for $\text{K}_{1-x}\text{Rb}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Figure S6. X-ray diffraction data for $\text{K}_{1-x}\text{Cs}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Differential scanning calorimetry data

Figure S7. Differential scanning calorimetry (DSC) data for parent compounds $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li, Na, K}$) from room temperature to 1000 °C.

Figure S8. DSC data of $\text{Li}_{1-x}\text{Na}_x\text{La Nb}_2\text{O}_7$ solid solution series ($0 \leq x \leq 1.0$) from room temperature to 1000 °C.

X-ray diffraction data for thermal analysis decomposition products

Figure S9. X-ray powder diffraction data for decomposition products for the series $\text{Li}_{1-x}\text{Na}_x\text{La Nb}_2\text{O}_7$. These are shown versus reference patterns for LiNbO_3 , NaNbO_3 and LaNbO_4 .

Figure S10. (a) X-ray powder diffraction data for decomposition products for $\text{Na}_{0.75}\text{K}_{0.25}\text{La Nb}_2\text{O}_7$ relative to NaNbO_3 , LaNbO_4 , and $\text{KLa Nb}_2\text{O}_7$. (b, c) Diffraction data from HTXRD at 500 °C, before and after heating to 1000 °C, for (b) $\text{Na}_{0.50}\text{K}_{0.50}\text{La Nb}_2\text{O}_7$ and (c) $\text{Na}_{0.25}\text{K}_{0.75}\text{La Nb}_2\text{O}_7$.

Raman data

Figure S11. Raman spectra for parent compounds $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li, Na, K, Rb, Cs}$).

Figure S12. Raman spectra for $\text{Li}_{1-x}\text{Na}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Figure S13. Raman spectra for $\text{Na}_{1-x}\text{K}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Figure S14. Raman spectra for $\text{K}_{1-x}\text{Rb}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Figure S15. Raman spectra for $\text{K}_{1-x}\text{Cs}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Figure S16. Raman spectra of $\text{Rb}_{1-x}\text{Cs}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

Tables

Table S1. Reaction conditions for parent compounds $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li, Na, K, Rb, Cs}$) and solid solutions $\text{A}_{1-x}\text{A}'_x\text{La Nb}_2\text{O}_7$ ($A/A' = \text{Li, Na, K, Rb, Cs}$).

Table S2. Unit cell parameters for $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li, Na, K, Rb, Cs}$) parent compounds.

Table S3. Summary of Raman data of apical Nb-O bond within the $\text{A}_{1-x}\text{A}'_x\text{La Nb}_2\text{O}_7$ ($A/A' = \text{Li, Na, K, Rb, Cs}$, $0 \leq x \leq 1$) solid solutions compounds.

1. Synthetic Conditions

Table S1. Reaction conditions for parent compounds $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li, Na, K, Rb, Cs}$) and solid solutions $\text{A}_{1-x}\text{A}'_x\text{La Nb}_2\text{O}_7$ ($A/A' = \text{Li, Na, K, Rb, Cs}$).

Compound		Reaction Method	Reaction Conditions (°C, h)*
$\text{LiLa Nb}_2\text{O}_7$		Ion Exchange from $\text{RbLa Nb}_2\text{O}_7 + \text{LiNO}_3$	325°C, 72 h
$\text{Li}_{1-x}\text{Na}_x$	0.25	Synthesis using stoichiometric amounts of $\text{LiLa Nb}_2\text{O}_7$ and $\text{NaLa Nb}_2\text{O}_7$	325°C, 72 h
	0.50		
	0.75		
$\text{NaLa Nb}_2\text{O}_7$		Ion Exchange from $\text{RbLa Nb}_2\text{O}_7 + \text{NaNO}_3$	350°C, 72 h
$\text{Na}_{1-x}\text{K}_x$	0.25	Synthesis using stoichiometric amounts of $\text{NaLa Nb}_2\text{O}_7$ and $\text{KLa Nb}_2\text{O}_7$	350°C, 72 h
	0.50		
	0.75		
$\text{KLa Nb}_2\text{O}_7$		Ion Exchange from $\text{RbLa Nb}_2\text{O}_7 + \text{KNO}_3$	380°C, 72 h
$\text{K}_{1-x}\text{Rb}_x$	0.25	Synthesis using stoichiometric amounts of $\text{KLa Nb}_2\text{O}_7$ and $\text{RbLa Nb}_2\text{O}_7$	400°C, 72 h
	0.50		
	0.75		
$\text{RbLa Nb}_2\text{O}_7$		Direct Synthesis from RbCO_3 , Nb_2O_5 , and La_2O_3	850°C, 24 h; 1050°C, 48 h
$\text{Rb}_{1-x}\text{Cs}_x$	0.25	Synthesis using stoichiometric amounts of $\text{RbLa Nb}_2\text{O}_7$ and $\text{CsLa Nb}_2\text{O}_7$	400°C, 72 h
	0.50		
	0.75		
$\text{CsLa Nb}_2\text{O}_7$		Direct Synthesis from CsCO_3 , Nb_2O_5 , and La_2O_3	1050°C, 48 h
$\text{KLa Nb}_2\text{O}_7$		Ion Exchange from $\text{RbLa Nb}_2\text{O}_7 + \text{KNO}_3$	380°C, 72 h
$\text{K}_{1-x}\text{Cs}_x$	0.25	Synthesis using stoichiometric amounts of $\text{KLa Nb}_2\text{O}_7$ and $\text{CsLa Nb}_2\text{O}_7$	600°C, 72 h
	0.50		
	0.75		
$\text{CsLa Nb}_2\text{O}_7$		Direct Synthesis from CsCO_3 , Nb_2O_5 , and La_2O_3	1050°C, 48 h

*All reactions carried out in air.

2. Parent ANb_2O_7 (A = Li, Na, K, Rb, Cs) X-ray Diffraction data

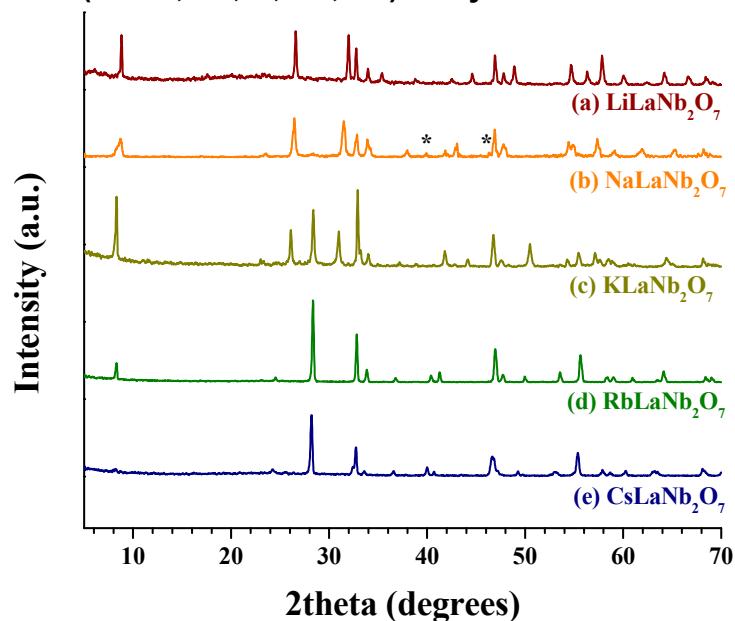


Figure S1. X-ray diffraction data for ANb_2O_7 for (a) $LiNb_2O_7$, (b) $NaNb_2O_7$ (taken at 300°C, *indicates Pt peaks from High-temperature XRD stage), (c) KNb_2O_7 , (d) $RbNb_2O_7$, and (e) $CsNb_2O_7$.

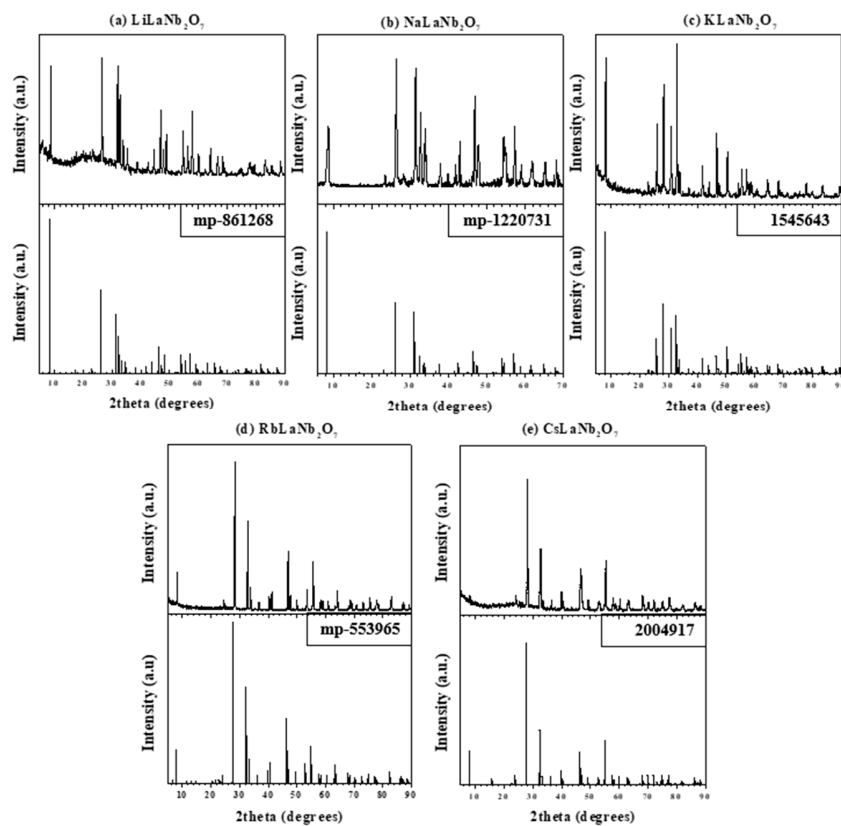


Figure S2. X-ray diffraction data (above) with reference patterns (below) for parent compounds, $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li}, \text{Na}^*, \text{K}, \text{Rb}, \text{Cs}$) (*collected at 300°C).

Table S2. Unit cell parameters for $\text{ALa Nb}_2\text{O}_7$ ($A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) parent compounds.

Unit Cell Parameters for $\text{ALa Nb}_2\text{O}_7$ Parent Compounds										
A	Experimental Values					Literature Values				
	a (Å)	b (Å)	c (Å)	V (Å ³)	Layer**	a (Å)	b (Å)	c (Å)	V (Å ³)	Ref.
Li	3.893(2)	-	20.435(8)	309.8(2)	S	3.8799(1)	-	20.3606(5)	306.50	[8]
Na*	3.900(4)	-	21.183(2)	322.2(6)	S	3.9022(1)	-	21.1826(8)	322.55	[9]
K	3.899(1)	21.658(8)	3.888(1)	328.4(2)	PS	3.9060(1)	21.6030(7)	3.8879(1)	328.07	[10]
Rb	3.8858(3)	-	10.991(1)	165.95(3)	E	3.885(2)	-	10.989(3)	165.86	[6]
Cs	3.906(1)	-	11.160(3)	170.26(8)	E	3.908(1)	-	11.160(4)	170.44	[7]

*To eliminate any possible hydration, XRD data were collected at 300 °C. **Layer orientation: staggered (S), partially staggered (PS), and eclipsed (E).

3. Solid Solution $\text{A}_{1-x}\text{A}'_x\text{La Nb}_2\text{O}_7$ ($A/A' = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) X-ray Diffraction Data

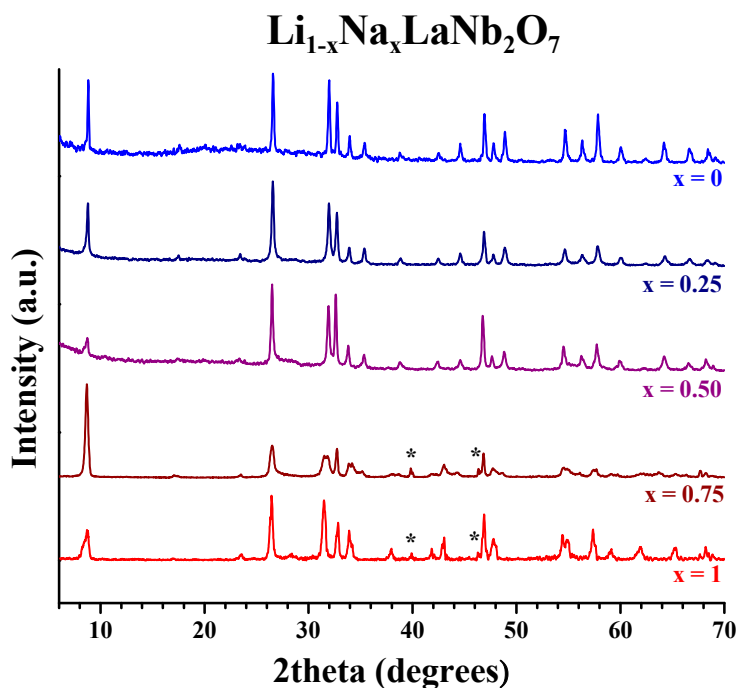


Figure S3. X-ray diffraction data for $\text{Li}_{1-x}\text{Na}_x\text{La Nb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series. Data for $x = 0.75$ and $x = 1$ were collected at 300°C. (* indicate Pt peaks from HTXRD stage).

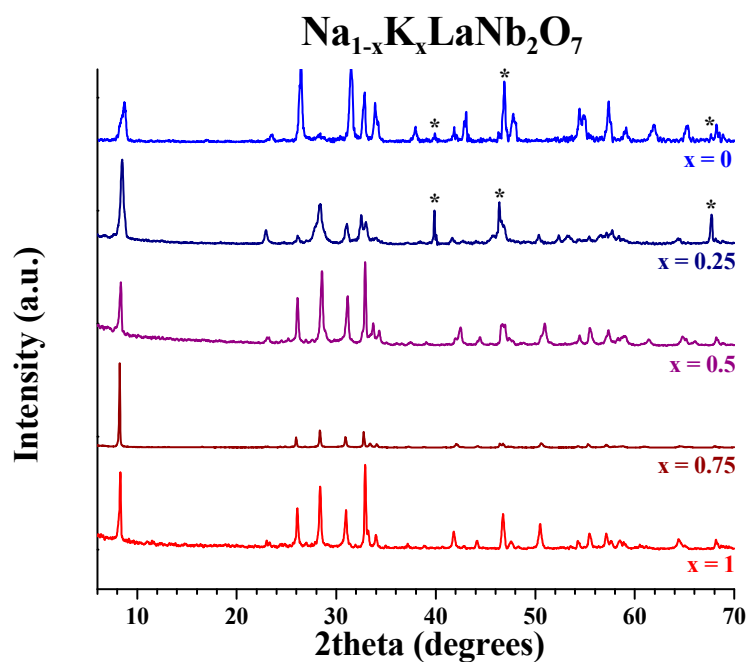


Figure S4. X-ray diffraction data for $\text{Na}_{1-x}\text{K}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series. Data for $x = 0$ and $x = 0.25$ were collected at 300°C (* indicate Pt peaks from HTXRD stage).

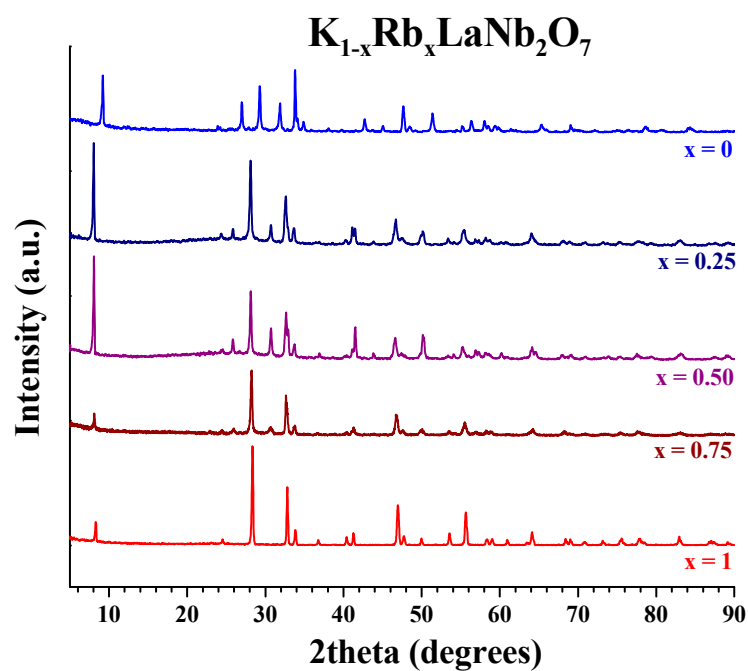


Figure S5. X-ray diffraction data for $\text{K}_{1-x}\text{Rb}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

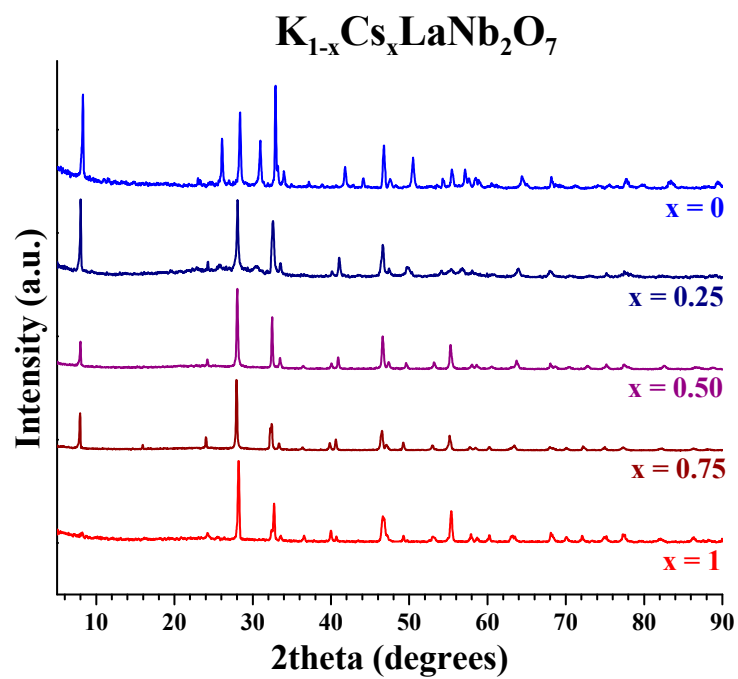


Figure S6. X-ray diffraction data for $\text{K}_{1-x}\text{Cs}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

4. DSC Data of Parent Compounds, ALaNb_2O_7 ($\text{A} = \text{Li, Na, K}$) and $\text{Li}_{1-x}\text{Na}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$)

Figure S7 shows DSC data of ALaNb_2O_7 ($\text{A} = \text{Li, Na, K}$). The metastable compounds $\text{LiLaNb}_2\text{O}_7$ and $\text{NaLaNb}_2\text{O}_7$ showed characteristic exothermic decomposition peaks at 719 °C and 812 °C respectively, while KLaNb_2O_7 showed no decomposition over the range of temperatures tested.

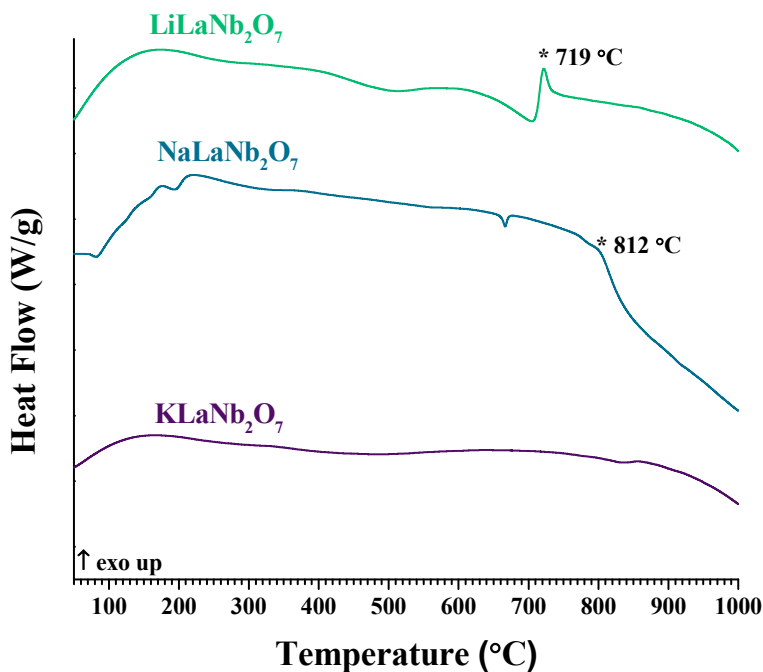


Figure S7. DSC data for parent compounds ALaNb_2O_7 ($\text{A} = \text{Li, Na, K}$) from room temperature to 1000 °C at a heating rate of 5 °C/min under Ar atmosphere. Decomposition temperatures (*) are shown for $\text{LiLaNb}_2\text{O}_7$ and $\text{NaLaNb}_2\text{O}_7$. Small low temperature endotherms (< 200 °C) for $\text{NaLaNb}_2\text{O}_7$ are due to the loss of water of hydration and the endotherm at 680 °C has been attributed to a structure change in the perovskite layer (Sato et al., *Solid State Ionics* 1992, 57, 285-293). KLaNb_2O_7 is stable above 1000 °C. (KLaNb_2O_7 , as well as $\text{RbLaNb}_2\text{O}_7$ and $\text{CsLaNb}_2\text{O}_7$, are all synthesized above 1000 °C.)

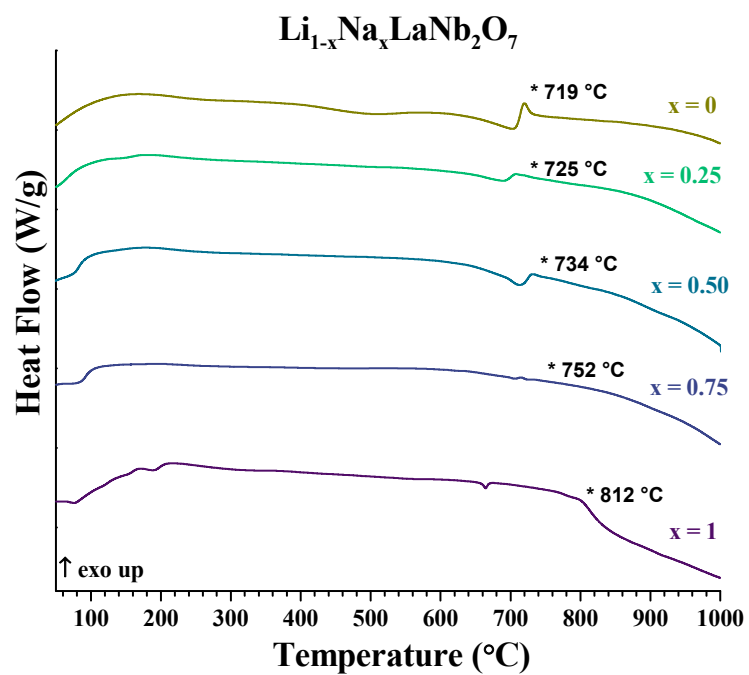


Figure S8. DSC data of $\text{Li}_{1-x}\text{Na}_x\text{LaNb}_2\text{O}_7$ solid solution series from room temperature to 1000 °C at a heating rate of 5°C/min under Ar atmosphere.

5. X-ray Powder Diffraction of Thermal Decomposition Products

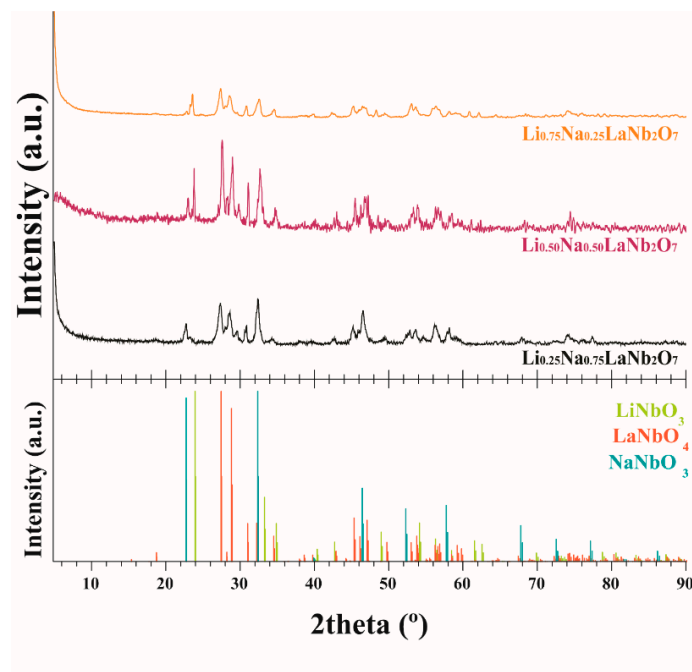
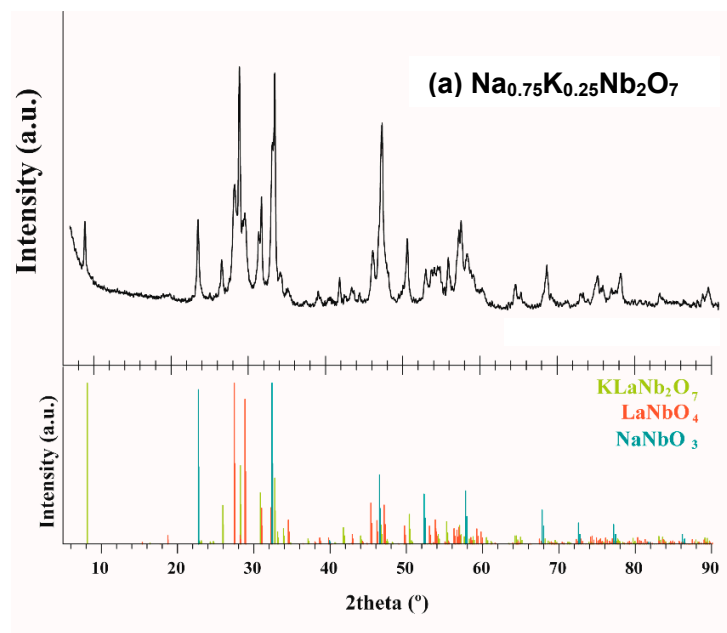


Figure S9. X-ray powder diffraction data for decomposition products for the series $\text{Li}_{1-x}\text{Na}_x\text{LaNb}_2\text{O}_7$. These are shown versus references for LiNbO_3 , NaNbO_3 and LaNbO_4 .



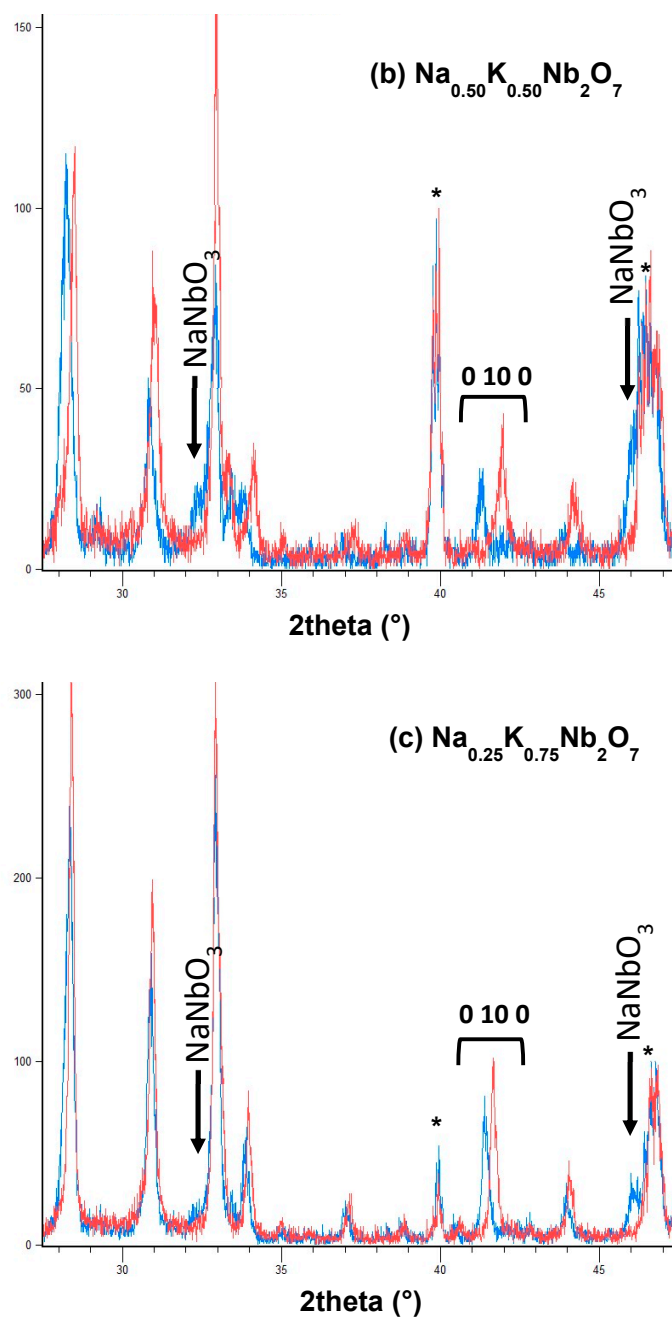


Figure S10. (a) X-ray powder diffraction data for $\text{Na}_{0.75}\text{K}_{0.25}\text{LaNb}_2\text{O}_7$ decomposition products relative to NaNbO_3 , LaNbO_4 , and KLaNb_2O_7 . (b,c) Diffraction data from HTXRD at 500 °C, before heating (red) and after heating to 1000 °C (blue); (b) $\text{Na}_{0.50}\text{K}_{0.50}\text{LaNb}_2\text{O}_7$ and (c) $\text{Na}_{0.25}\text{K}_{0.75}\text{LaNb}_2\text{O}_7$; crystalline decomposition products are much less apparent than in (a), however, the shift of the $0\ 10\ 0$ reflection pertinent to the perovskite layer spacing can be seen. (*) indicates Pt peak from high temperature stage.)

6. Raman Spectroscopy Data of Parent Compounds ALaNb_2O_7 ($\text{A} = \text{Li, Na, K, Rb, Cs}$) and $\text{A}_{1-x}\text{A}'_x\text{LaNb}_2\text{O}_7$ ($\text{A/A}' = \text{Li, Na, K, Rb, Cs}$)

Table S3. Summary Raman data of apical Nb-O bond within the $\text{A}_{1-x}\text{A}'_x\text{LaNb}_2\text{O}_7$ ($\text{A/A}' = \text{Li, Na, K, Rb, Cs}$; $0 \leq x \leq 1$) solid solutions compounds.

Compound		Apical Nb-O bond vibration (cm^{-1})
$\text{LiLaNb}_2\text{O}_7$		943
$\text{Li}_{1-x}\text{Na}_x$	0.25	939
	0.50	934
	0.75	933
$\text{NaLaNb}_2\text{O}_7$		933
$\text{Na}_{1-x}\text{K}_x$	0.25	927
	0.50	926
	0.75	925
KLaNb_2O_7		929
$\text{K}_{1-x}\text{Rb}_x$	0.25	927
	0.50	928
	0.75	927
$\text{RbLaNb}_2\text{O}_7$		930
$\text{Rb}_{1-x}\text{Cs}_x$	0.25	928
	0.50	927
	0.75	927
$\text{CsLaNb}_2\text{O}_7$		926
KLaNb_2O_7		929
$\text{K}_{1-x}\text{Cs}_x$	0.25	927
	0.50	927
	0.75	927
$\text{CsLaNb}_2\text{O}_7$		926

Raman spectra for all parent compounds are shown in **Figure S11**, while the solid solutions are shown in **Figures S12 - S16**.

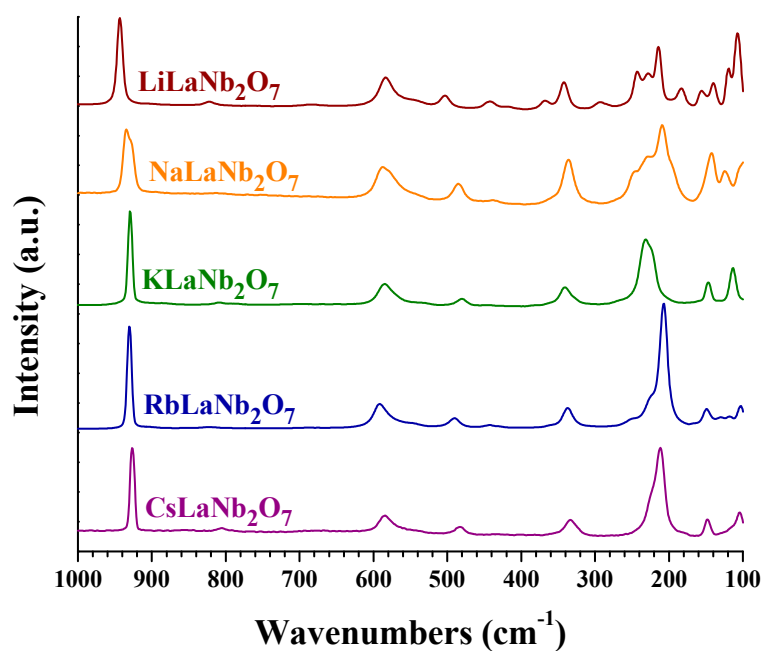


Figure S11. Raman spectra for parent compounds ALaNb_2O_7 ($A = \text{Li, Na, K, Rb, Cs}$).

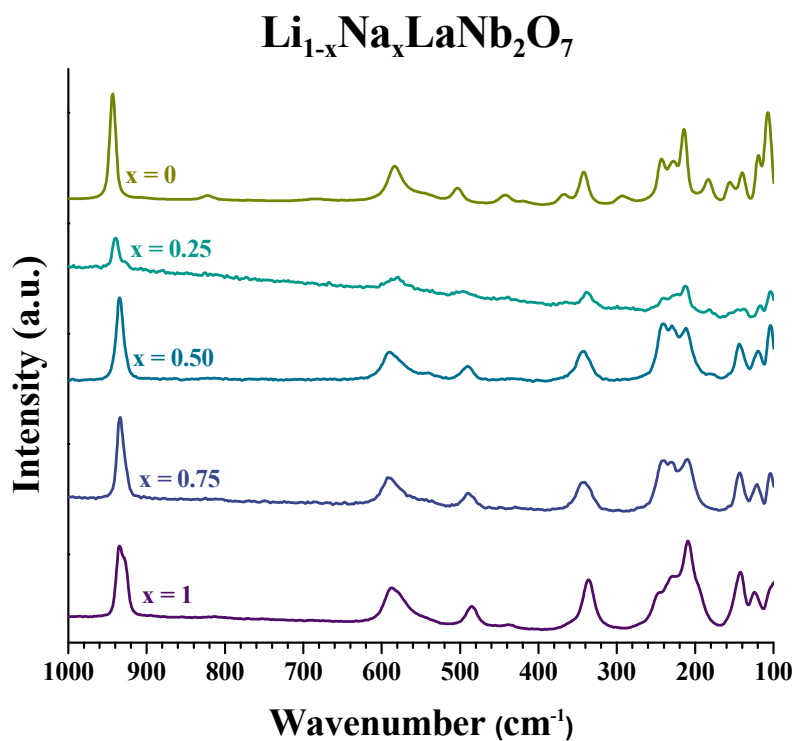


Figure S12. Raman spectra for $\text{Li}_{1-x}\text{Na}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

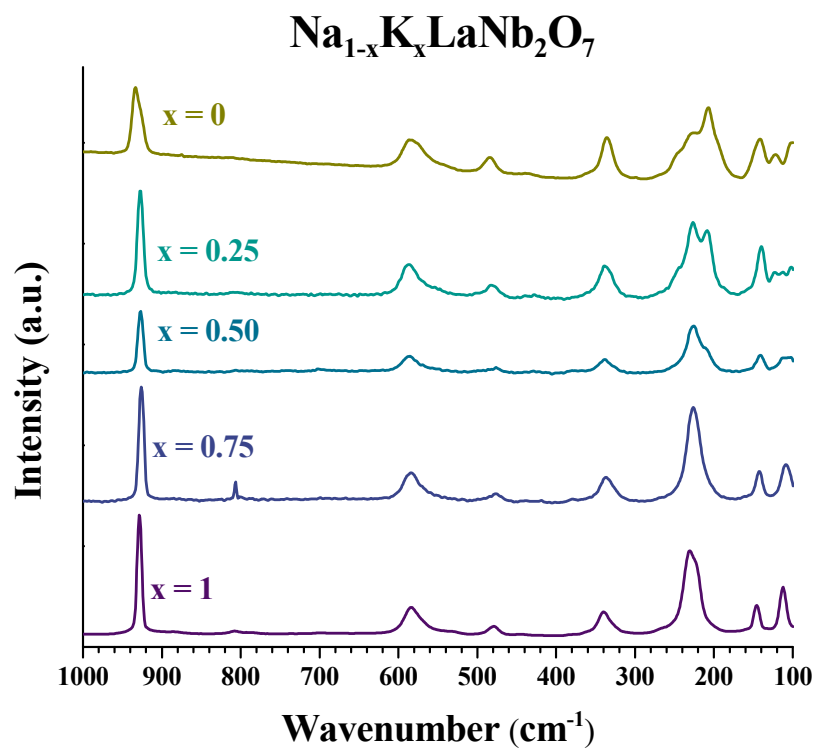


Figure S13. Raman spectra for $\text{Na}_{1-x}\text{K}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

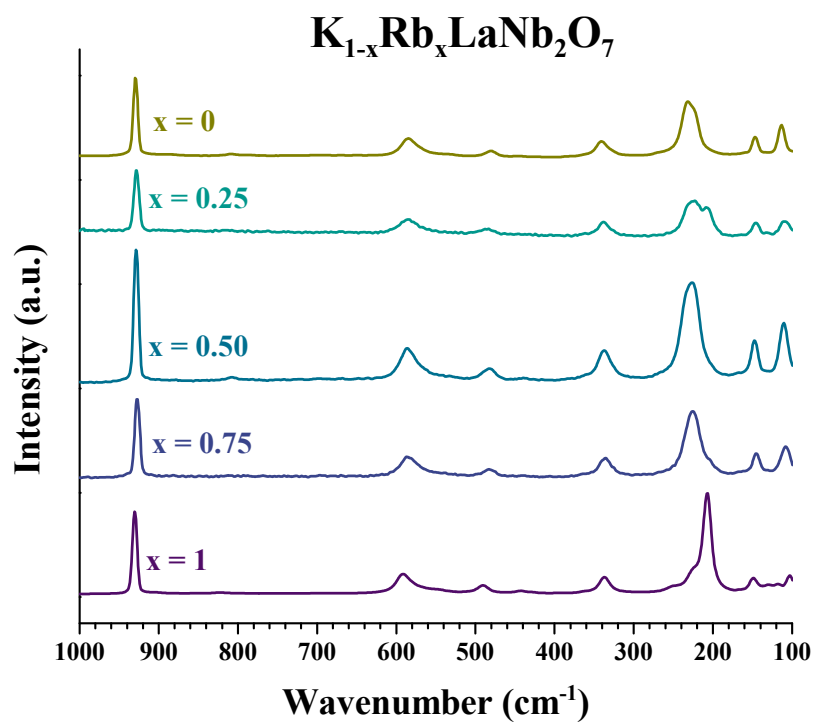


Figure S14. Raman spectra for $\text{K}_{1-x}\text{Rb}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

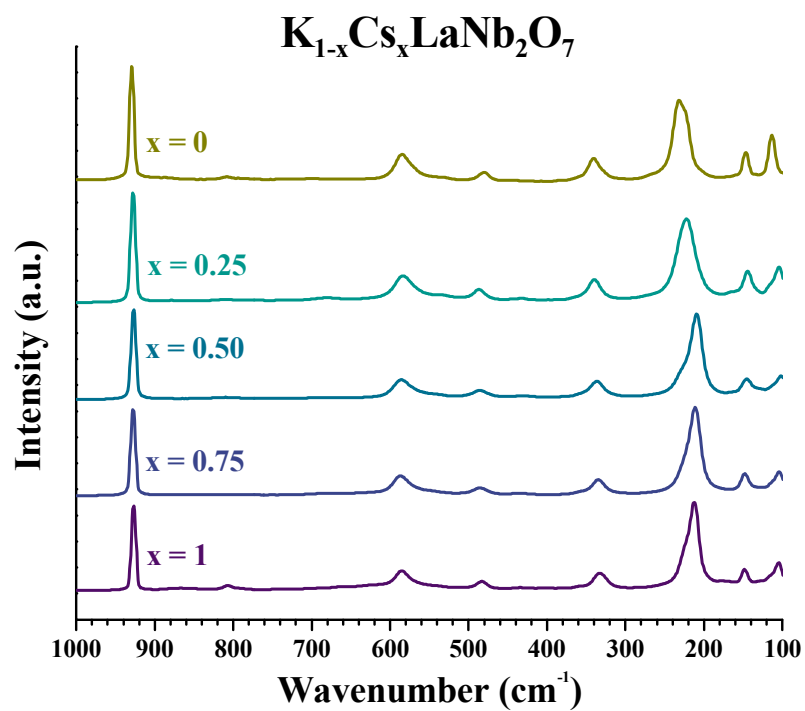


Figure S15. Raman spectra for $\text{K}_{1-x}\text{Cs}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.

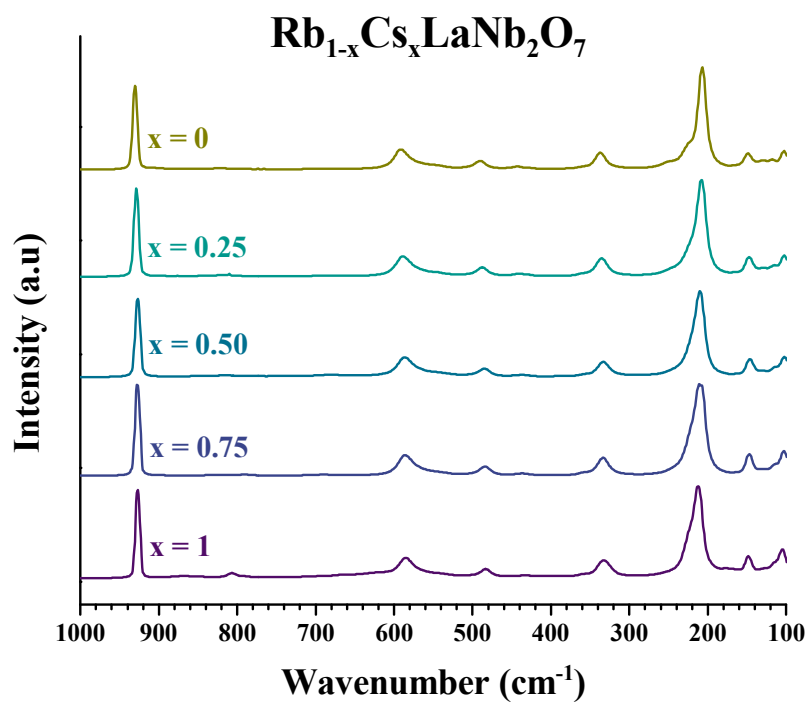


Figure S16. Raman spectra of $\text{Rb}_{1-x}\text{Cs}_x\text{LaNb}_2\text{O}_7$ ($0 \leq x \leq 1$) solid solution series.