

Article

Layer Alignment via Short Strong Hydrogen Bonding in the Dion–Jacobson Perovskite Solid Acid HLaNb_2O_7

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Abstract

The Dion–Jacobson perovskite solid acid, HLaNb_2O_7 , is an important intermediate in many topochemical reactions such as those involving ion exchange, intercalation, exfoliation, and grafting. Rietveld structure refinement of time-of-flight neutron diffraction data (7.66 K, $P4/mmm$, $a = b = 3.8907(3)$ Å, $c = 10.5068(9)$ Å) shows that protons bridging across the HLaNb_2O_7 interlayer serve to align LaNb_2O_7 blocks through NbO_6 apical oxygens. The oxygens are 2.54 Å apart, with the intermediate proton distributed over two half-occupied sites, and 1.15(10) Å from the closest oxygen. Such short strong hydrogen bonds are shorter (1.40 Å) than are typical for many known mixed metal oxide solid acids (ca. 2.8 Å–3.5 Å). Anisotropic refinement of the hydrogen thermal parameter reveals an elongation suggesting an active hydrogen that moves between the two oxygens, $\text{O}-\text{H} \cdots \text{O} \leftrightarrow \text{O} \cdots \text{H}-\text{O}$; DFT modeling supports this behavior, finding a minimal activation energy between two states; and infrared studies (FTIR) exhibit a broad low-energy band at ~ 1600 cm^{-1} , associated with the hydrogen resonance between the apical oxygens. These results are discussed in terms of structure, strong low-barrier hydrogen bonding, and proton mobility.

Keywords: Dion–Jacobson; layered perovskites; ion exchange; solid acid; hydrogen bonding; DFT



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1. Introduction

The foundational importance of hydrogen interactions is demonstrated throughout the natural and synthetic world, where hydrogen bonding is requisite for various critical functions within biological systems, water chemistry, materials properties, etc. [1–5]. Further, the mobility of protons is essential to pH regulation within living systems as well as in ion-active technologies and key synthetic processes [6–9]. In terms of mixed metal oxides, select fuel cells and catalysts rely on proton migration through oxide lattices. A series of doped barium oxide solid acids ($\text{BaB}_{1-x}\text{B}'_x\text{O}_{3-x/2-y}(\text{OH})_{2y}$, $\text{B} = \text{Zr, Ce, Tb, Th}$; $\text{B}' = \text{Y, Yb, In}$), for example, offer high proton conduction, acting as key components in fuel cells [10], and important niobium oxide acid catalysts (e.g., HNbO_5 ($\text{B} = \text{Ti, Mo, W}$)) are active for esterification, elimination, and dealkylation reactions [11,12]. Pivotal to the

performance of these sets of materials is the hydrogen–oxygen interactions (O...H) within their extended structures.

Dion–Jacobson type layered perovskites, $A'[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$, where A' is a monovalent cation such as an alkali metal ion or a proton, A is an alkaline earth metal, rare earth, or main group element, B is a transition metal, and n is the number of octahedral layers, have been extensively studied for a variety of applications [13–15]. Especially of interest is the extensive topochemical flexibility of these materials, leading to a series of new compounds through intercalation, ion exchange, and grafting reactions [16–18]. $\text{RbLaNb}_2\text{O}_7$ is illustrative of this behavior where tailored products readily result from intercalation ($\text{Rb}_2\text{LaNb}_2\text{O}_7$, $(\text{Rb}_2\text{Cl})\text{LaNb}_2\text{O}_7$, $(\text{Li}_2\text{Cl})\text{LaNb}_2\text{O}_7$, $(\text{Rb}_2\text{YH})\text{LaNb}_2\text{O}_7$ ($\text{Y} = \text{O}, \text{S}, \text{Se}$)) [19–23], ion exchange (ALaNb_2O_7 ($\text{A} = \text{K}, \text{Na}, \text{Li}, \text{H}, \text{NH}_4, \text{Ag}, \text{and H}$), $(\text{CuX})\text{LaNb}_2\text{O}_7$ ($\text{X} = \text{Cl}, \text{Br}$), $(\text{MCl})\text{LaNb}_2\text{O}_7$ ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{and Co}$)) [24–26], and grafting reactions that produce inorganic/organic hybrids including $(\text{C}_n\text{H}_{2n+1})\text{LaNb}_2\text{O}_7$ ($n = 1\text{--}12$) and RLaNb_2O_7 where R can be alkenes, chlorohydrosilanes, polyethers, organophosphonic acids, glucopyranose, and hydroxyaromatics [27,28]. Additional significance is seen where derivatives of HLaNb_2O_7 can undergo exfoliation, leading to various dispersed nanosheets [29–32].

The solid acid, HLaNb_2O_7 , is an important compound in a variety of reactions involving a number of interlayer modifications. Readily produced from $\text{RbLaNb}_2\text{O}_7$ by a simple ion exchange with dilute acids, it serves as a key intermediate to inorganic/organic hybrids formed via grafting reactions, to intercalation reactions, exfoliation reactions, as well as the formation of a blue-bronze derivative [24,27,32,33]. First reported by Gopalakrishnan and coworkers [24], the compound can be made anhydrous or exist as a hydrate; Sato et al. treated the acid under 100% humidity at 25 °C to obtain the composition $\text{HLaNb}_2\text{O}_7 \cdot 0.5 \text{H}_2\text{O}$ [34]. Proton conductivity has been investigated in these systems, where they were found to follow a Freundlich-type isotherm [31,34]. HLaNb_2O_7 is recognized as a Brønsted acid and has been shown to readily react with various amines; such intercalation reactions have led to the series $(\text{C}_n\text{H}_{2n+1}\text{NH}_2)\text{LaNb}_2\text{O}_7$ ($n = 1\text{--}8$) [27]. Further, composite materials involving HLaNb_2O_7 have been shown to be active photocatalysts [35], while others have exhibited significant band gap reduction upon the formation of a reduced carbon component within the host [36].

Structural characterization of HLaNb_2O_7 has included X-ray diffraction, NMR, and Raman studies. Based on unit cell analysis, Gopalakrishnan, Bhat, and Raveau suggested that the compound had aligned perovskite layers [24]. The structure refinement of X-ray powder diffraction data by Sato and coworkers confirmed this layer orientation [37], and additional studies by this team on temperature-dependent conduction showed that, unlike the alkali metal compounds, ALaNb_2O_7 ($\text{A} = \text{Li}, \text{Na}, \text{K}$), HLaNb_2O_7 exhibited two distinct transport regions with low temperature behavior influenced by hydration [37]. Solid-state NMR showed a single proton resonance in anhydrous HLaNb_2O_7 [38], and Raman spectroscopic studies indicated that the apical Nb–O bond strength was stronger than that seen in any of the alkali metal cation series (ALaNb_2O_7 , $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) [28,39]. Though these various studies provide insight on this material, a direct determination of the proton location within the perovskite interlayer has not been reported.

Herein we report on the structure and modeling of HLaNb_2O_7 . Neutron studies were utilized to determine the hydrogen position where the H was found to be statistically distributed between two sites intermediate to the apical oxygens of aligned perovskite layers. DFT modeling studies are consistent with diffraction and show that the energy variation between the two sites is relatively flat. Infrared studies further support this behavior and are consistent with strong low-barrier hydrogen bonding. The importance of this result is discussed with regard to its impact on the layered perovskite structure, hydrogen bonding, and what this indicates about proton mobility in such materials.

2. Experimental Section

Reagents: Rb_2CO_3 (Alfa Aesar, 99.8%) was purchased from Alfa Aesar (Alfa Aesar, Ward Hill, MA, USA, 99.8%) and used as received. Nb_2O_5 (Alfa Aesar, 99.9985%) and La_2O_3 (Alfa Aesar, 99.99%) were heated at 1000 °C in air for 12 h to remove any impurities. Nitric acid (Alfa Aesar, 99+%) was used without further purification.

RbLaNb₂O₇: For synthesis of $\text{RbLaNb}_2\text{O}_7$, Rb_2CO_3 , La_2O_3 , and Nb_2O_5 were taken in the molar ratio of 1.3:1:2, respectively [24]. The mixture was thoroughly ground and pre-heated at 850 °C for 12 h, reground, and then heated at 1050 °C for 24 h, followed by grinding and reheating at 1100 °C for 24 h.

Protonation: Proton exchange of $\text{RbLaNb}_2\text{O}_7$ was carried out with a 6 M HNO_3 solution via a microwave-assisted reaction for 3 h at 60 °C (maximum power of 300 W) with continuous stirring in a Milestone (Milestone Inc., Shelton CT, USA) StartSYNTH Microwave Synthesis Labstation. The reactions were executed in quartz pressure reactors (<15 bar) with a stirring bar and Weflon button (graphite-doped Teflon) on Milestone's START rotating platform. Caution: *Each quartz reactor vessel should be carefully inspected for glass defects before every reaction as these defects could result in hotspots, leading to explosions.* The product, HLaNb_2O_7 , was washed with distilled water and acetone until the pH reached 7; the sample was then dried at 130 °C for 3 h [40]. (Optical and SEM images of $\text{RbLaNb}_2\text{O}_7$ and HLaNb_2O_7 samples are shown in Figure S1.)

Characterization: X-ray powder diffraction (XRD) data were collected on a Philips X'Pert system equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a curved graphite monochromator. Raman spectra were obtained with a Thermo-Fisher (Thermo Fisher Scientific, Waltham, MA, USA) DXR dispersive Raman spectrometer using the $\lambda = 532 \text{ nm}$ line with a spectral resolution of 3 cm^{-1} . FTIR spectra were measured on an Agilent (Agilent Technologies, Santa Clara, CA, USA) Cary 630 FTIR Spectrometer fitted with a Diamond ATR sampling module. Neutron data were collected on the powder diffractometer POWGEN beam line at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). An amount of 0.5 g of anhydrous HLaNb_2O_7 was sealed in a vanadium can (6 mm diameter) and sent to the POWGEN facility via their mail-in program. Measurements were collected at 7.66 K. Rietveld analyses of the diffraction data were performed using GSAS II (General Structure Analysis System, v5.2.0) software [41]. Scanning electron microscopy (SEM) images were taken on the Phenom Pro Thermo-Fisher Scientific benchtop microscope.

Modeling: Density functional theory (DFT) calculations were carried out using the plane-wave self-consistent field program (pw.x) of the Quantum Espresso version 6.5 software package [42]. A $3 \times 3 \times 3$ Monkhorst–Pack reciprocal space grid was used in the Brillouin zone. The energy cutoff was 70 Rydberg for the plane waves and 300 Rydberg for the charge density. The energy convergence with respect to all parameters was checked. The convergence threshold for self-consistency of the total energy is 10^{-6} Rydberg. The lattice parameters and atomic positions were minimized until the total energy changed by less than 10^{-4} Rydberg and the forces by less than 10^{-3} Rydberg/Bohr. Results were obtained with the PBE-SOL functional [43]. Projector Augmented Wave (PAW) pseudopotentials [44] were used, generated by the AUTOMPAW code [45] for the PBE-SOL functional with scalar relativistic formalism [46], core corrections, and 1500 logarithmic grid points. Calculations were also carried out with the addition of dispersion interactions using the Grimme-D2 method [47]. The calculations used the stoichiometry HLaNb_2O_7 , so assuming a single occupancy for the hydrogen atom.

3. Results

Proton exchange of $\text{RbLaNb}_2\text{O}_7$ readily produces the solid acid, HLaNb_2O_7 . X-ray diffraction patterns of HLaNb_2O_7 and $\text{RbLaNb}_2\text{O}_7$ are shown in Figure 1. A clear reduction

in the interlayer spacing with structure retention can be seen for HLaNb_2O_7 , compared with $\text{RbLaNb}_2\text{O}_7$, as the 001 reflection shifts to higher angles. Data are consistent with the literature where the eclipsed conformation of the layers is maintained with a contraction of about 0.5 Å [24].

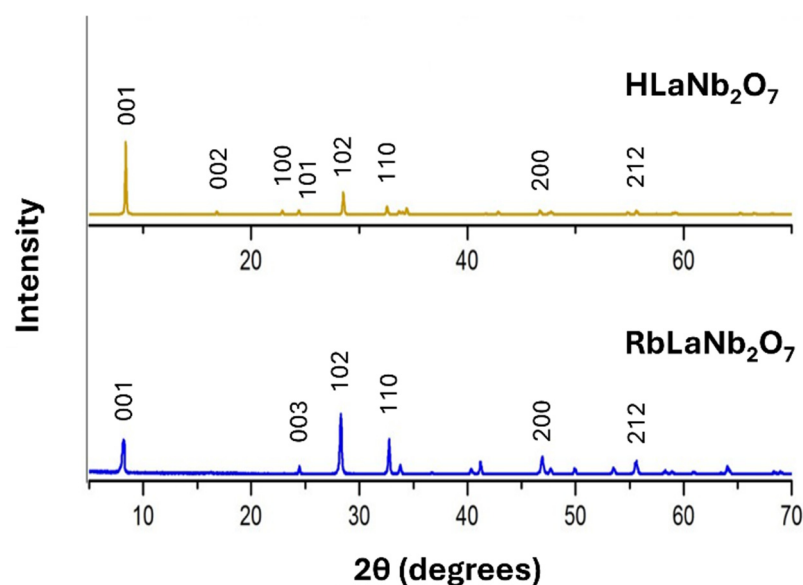


Figure 1. XRD pattern of HLaNb_2O_7 compared with $\text{RbLaNb}_2\text{O}_7$. Select reflections (hkl) are labeled based on tetragonal cell [24].

Neutron diffraction: Rietveld refinement was performed on HLaNb_2O_7 neutron diffraction data. For the analysis, refinement started with the $P4/mmm$ space group and the aristotype space group for both $\text{RbLaNb}_2\text{O}_7$ and $\text{CsLaNb}_2\text{O}_7$ [48]. The positions of the atoms in the LaNb_2O_7 block were easily determined due to the topochemical nature of the proton exchange. To establish an effective starting point for the hydrogen, a Fourier image was obtained (Figure S2), and this mapping showed additional nuclear density between the two apical oxygens in the interlayer. It is known that the average O–H bond distances in solids are typically 0.9–1.1 Å [49]. Since the two oxygens were ~2.6 Å apart, one would not expect the hydrogen to reside at the exact midpoint because the O–H bond length would be too long. Comparison of the two models, one where the hydrogen is centrally located at 1 d (0.5, 0.5, 0.5) and the other where hydrogen is distributed equally over equivalent 2 h sites (0.5, 0.5, z), supported this expectation, as the 2 h model gave the better fit (R_{wp} : 10.772 versus 0.9726, respectively). The Rietveld refinement of the TOF neutron diffraction data is shown in Figure 2, and the atomic positions and the bond lengths for HLaNb_2O_7 are shown in Tables 1 and 2, respectively. The bond length for O–H was found to be 1.15 Å. Anisotropic thermal parameter refinement was performed on H to reveal an elongation of the thermal ellipsoids between the two oxygens. The resulting structure for HLaNb_2O_7 is presented in Figure 3.

Vibrational spectroscopy: The vibrational spectra of HLaNb_2O_7 were examined by both Raman and FTIR. Raman data for HLaNb_2O_7 and $\text{RbLaNb}_2\text{O}_7$ are shown (Figure 4). No features are observed in the O–H region above 1000 cm^{-1} . Low-energy vibrations below 700 cm^{-1} are ascribed to inner-layer vibrations of the perovskite block [28,50–52]. The vibration around 930 cm^{-1} is attributed to the A_{1g} stretch of the apical Nb–O oxygen and is consistent with previous reports [28]. This band is found to shift to higher energies in HLaNb_2O_7 versus $\text{RbLaNb}_2\text{O}_7$. A similar blue shift in the A_{1g} band is also apparent when comparing HLaNb_2O_7 to other members of the series ALaNb_2O_7 ($A = \text{Li–Cs}$, Table S1).

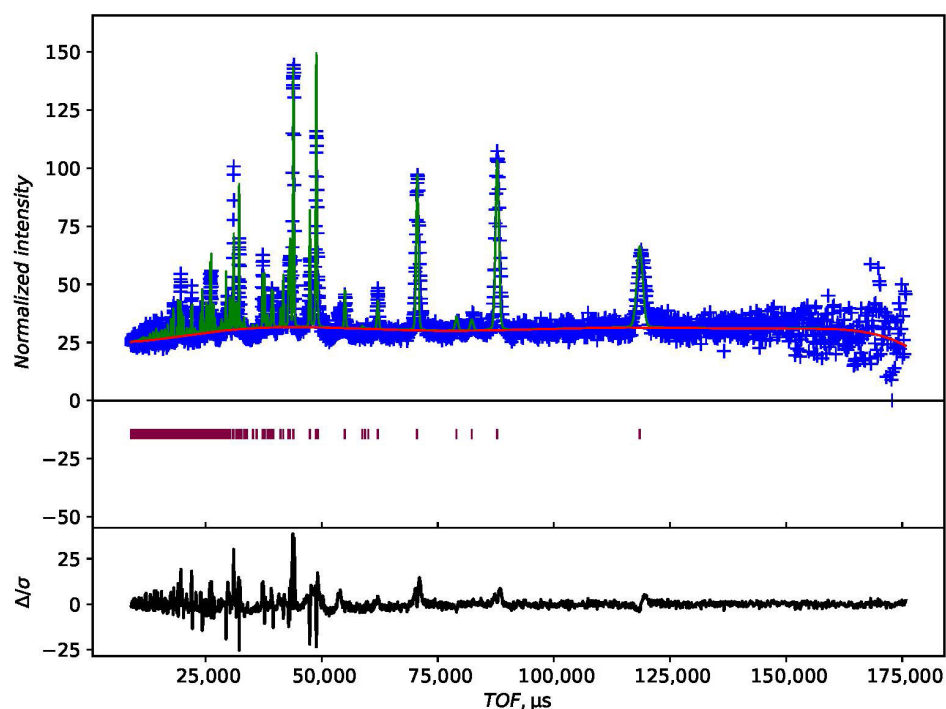


Figure 2. Rietveld refinement of HLaNb₂O₇. Observed data are represented by blue crosses, the calculated data are shown as solid green line, background fit in red, reflection tick marks in maroon, and the difference plot in black at the bottom.

Table 1. Crystallographic data from neutron structure refinement of HLaNb₂O₇ *.

Atom	Position	x	y	z	Occupancy	Uiso	U11	U22	U33
La	1a	0	0	0	1	0.0156	-	-	-
Nb	2h	0.5	0.5	0.209(1)	1	0.0240	-	-	-
O1	1c	0.5	0.5	0	1	0.0302	-	-	-
O2	4i	0	0.5	0.1681 (7)	1	0.0170	-	-	-
O3	2h	0.5	0.5	0.379 (2)	1	0.0435	-	-	-
H	2h	0.5	0.5	0.488 (9)	0.5	-	0.0799	0.0799	0.1862

* Space group *P4/mmm*, $a = b = 3.8907(3)$ Å, $c = 10.5068(9)$ Å, $\text{vol} = 159.05(2)$ Å³, $R_p = 0.09413$, $R_{wp} = 0.09726$.

Table 2. Bond lengths and interatomic distances in HLaNb₂O₇.

Bond	Length, Å
H–O3	1.15 (10)
Nb–O3	1.79 (2)
Nb–O2	1.992 (3)
Nb–O1	2.192 (12)
La–O2	2.628 (5)
Interatomic distances	
H...O3'	1.40
O3...O3'	2.54

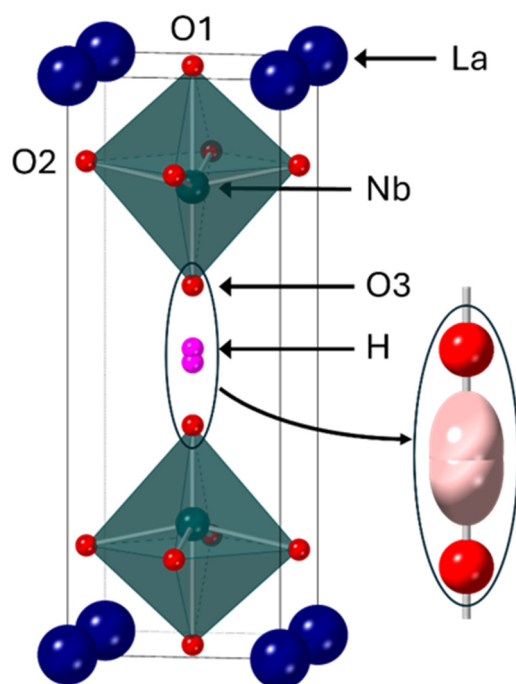


Figure 3. Structure of HLaNb₂O₇. Overlapping anisotropic thermal ellipsoids for the two hydrogen sites are shown in the inset.

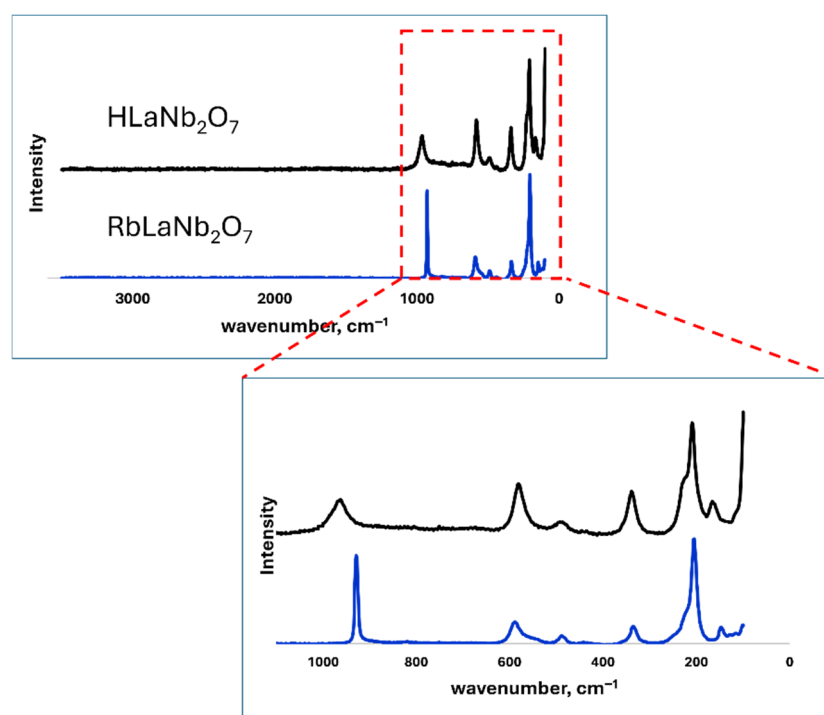


Figure 4. Raman data from 3500 to 100 cm^{−1} for both RbLaNb₂O₇ (blue) and HLaNb₂O₇ (black).

The FTIR spectra of HLaNb₂O₇ did not exhibit vibrational modes above 2800 cm^{−1}; a distinct broad feature, however, was observed at ~1600 cm^{−1} relative to RbLaNb₂O₇ (Figure S3). Such broad features can be attributed to strong hydrogen bonds. Other low-energy vibrations are consistent with many inner-layer vibrations as seen in RbLaNb₂O₇.

Modeling: Full unit cell geometry optimizations were carried out with the PBE-SOL functional (M-1, Table S2) and with the addition of dispersion interactions (M-2, Grimme-D2, Table S3). The two models are consistent with diffraction results and with each

other. Table 3 compares unit cell parameters, bond lengths, and interatomic distances in HLaNb_2O_7 for the three sets of results. Experimental values match more closely with the DFT model that includes dispersion corrections (M-2).

Table 3. Comparison of calculated (DFT) and observed unit cell parameters, bond lengths, and interatomic distances in HLaNb_2O_7 .

	a (Å)	c (Å)	O–H (Å)	O...O (Å)	O–H...O (Å)
M-1	3.879	10.387	1.12	2.36	1.24
M-2	3.822	10.556	1.16	2.52	1.36
Experimental	3.891	10.507	1.15	2.54	1.40

In the M-1 calculation, the two complementary positions for H between O3 and O3' correspond to bond distances of 1.12 Å and 1.24 Å, respectively. M-2 gave similar results with bond distances of 1.16 Å and 1.36 Å, respectively. Energy calculations relating to the hydrogen interaction with the apical oxygens of adjacent NbO_6 octahedra were carried out using Model 1 with the O–H distance constrained to a specific value and all other coordinates allowed to relax. This varies the position of the hydrogen along a coordinate between the O3 and O3' atoms. The energy versus O–H distance is shown in Figure 5. The energy well, as the hydrogen moves from one oxygen to the other, is flat, with essentially no barrier, indicating that the hydrogens are not localized on either oxygen with a typical O–H bond length. The barrier, at a distance of 1.2 Å, is 0.07 kcal/mol.

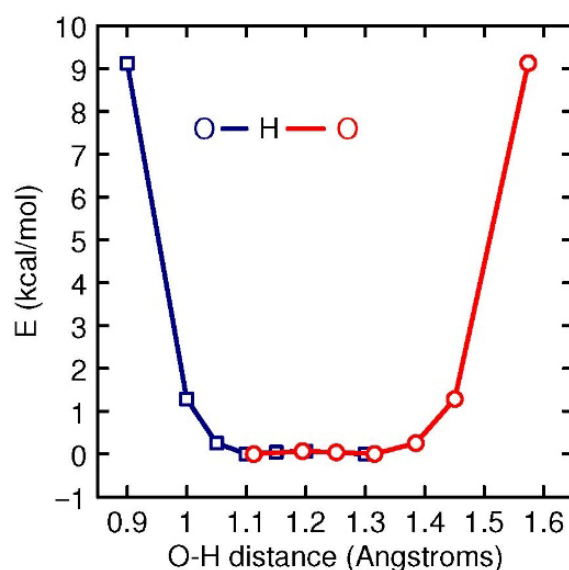


Figure 5. Energy versus distance for O–H in HLaNb_2O_7 . The blue line and squares show the O3–H distance, and the red line and circles show the O3'–H distance.

4. Discussion

Rietveld refinement of HLaNb_2O_7 neutron data confirms that the layers are in an eclipsed orientation with protons bridging across the adjacent apical oxygens of the NbO_6 octahedra. The hydrogens partially occupy two equal sites with an O–H distance of about 1.15 Å, a hydrogen bond (O–H...O) of 1.40 Å, and a distance between the pair of oxygen donor and acceptor ions (O...O) of 2.54 Å. Libowitzky [49] classified hydrogen bonds into three categories, where for donor–acceptor distances, “very strong” hydrogen bonds have O...O distances < 2.50 Å, “strong” hydrogen bonds are in the range of 2.50–2.70 Å, and “weak” bonds are > 2.70 Å. Jeffrey [53] classified similar features based on the bonding

characteristics, where the shortest hydrogen bonds were predominantly covalent in nature, the intermediate bonds had some electrostatic character, and the longer bonds were weak electrostatic interactions. The O...O distance observed in HLaNb₂O₇ is consistent with a strong to very strong hydrogen bond with significant covalency.

Hydrogen bonding also correlates to the energy of the O–H stretching frequency [49]. Typically, IR bands occur as broad peaks and can vary from ~3500 cm^{−1} for weak hydrogen bonds, all the way down to ~1000 cm^{−1} for very strong hydrogen bonds. In HLaNb₂O₇, a broad band is observed at 1610 cm^{−1}. Vibrational energies in this range have been associated with strong to very strong hydrogen bonds, O...O distances of about 2.5 Å, and O–H...O distances of about 1.45 Å [49]. The distances determined from our neutron diffraction study, 2.54 Å and 1.40 Å, respectively (Table 2), are consistent with this.

As the distance between donor and acceptor ions decreases, so does the magnitude of the energy barrier between the two states, O–H...O ↔ O...H–O. In HLaNb₂O₇, as shown by diffraction data, DFT calculations, and vibrational spectra, the oxygens are close enough that there is minimal energy required for a hydrogen to move back and forth between the two states, strongly indicating that the short strong bonds in this solid acid can be related to low-barrier hydrogen bonding (LBHB) [54]. Though typically associated with proteins and enzymes as possible drivers for important biological catalytic processes [55], short hydrogen bonds associated with LBHB can also occur in some mixed metal oxides [49].

Hydrogen bonding in layered mixed metal oxide solid acids can vary from short strong low-barrier interactions to localized hydrogens with weak hydrogen bonds. The nature of the bonding in these different systems is influenced by both composition and structure. Here we compare a series of layered oxides (Figure 6, Table 4) to HLaNb₂O₇. In HCoO₂ (Figure 6a), for example, CoO₂[−] layers of edge-sharing octahedra are tethered via bridging hydrogens akin to the delafossite structure [56]; the donor oxygen resides at the intersection of the three edge-sharing CoO₆ octahedra, leading to a strong covalent interaction with the oxygen. This, in turn, produces very strong hydrogen bonds with no barrier such that the proton resides at the midpoint between the two layers. In HTiNbO₅, the hydrogen bonding is only slightly weaker. In this corrugated structure (Figure 6b), the TiNbO₅[−] layers form from edge- and corner-sharing MO₆ (M = Ti/Nb) octahedra. Hydrogens bridge the interlayer, attached to edge-sharing oxygens (O–H, 1.18 Å) and hydrogen-bonding across the interlayer to adjacent apical oxygens (O–H...O, 1.335 Å) [57]. HLaNb₂O₇ (Figure 6c), in terms of its interlayer hydrogen bonding, shares features with both HCoO₂ and HTiNbO₅. Like HCoO₂, the hydrogens bridge across equivalent layer sites, but with regard to distances O–H...O, the bonding is more similar to HTiNbO₅ (Table 4). One might ask why the proton in HLaNb₂O₇ is not located exactly at the midpoint between the perovskite layers—this may be due to a lower covalency in the Nb–O–H linkage, possibly combined with a slight electrostatic repulsion between negatively charged perovskite layers. Other compounds, such as HNdTio₄ and kaolinite (H₄Al₂Si₂O₉), have far weaker hydrogen bonding. HNdTio₄ is also a perovskite-related compound (Ruddlesden–Popper type) with corner-sharing octahedra, but because of its composition, each of the apical oxygens in the interlayer has a proton (twice as many as in HLaNb₂O₇). Figure 6d shows an example of the localized protons on opposing apical oxygens in the interlayer. In HNdTio₄, the O–H distance is shorter than in the other oxides (1.038 Å), and the O–H...O distance is considerably longer (1.978 Å). (Note that the refinement of the proton structure in HNdTio₄ led to an 8-fold distribution of H's on each oxygen (site symmetry 16e) [58]—for clarity, only one of the hydrogens is shown on adjacent apical oxygens.) Kaolinite is quite different from these other solid acids in that the composition of its opposing layers is distinct (Figure 6e); the hydrogens are localized on an aluminum oxide layer (O–H, 0.976 Å) while weakly

bridging to the adjacent silicon oxide layer [59]. This compositionally asymmetric structure helps to drive nanosheet scrolling on the exfoliation of these compounds [60].

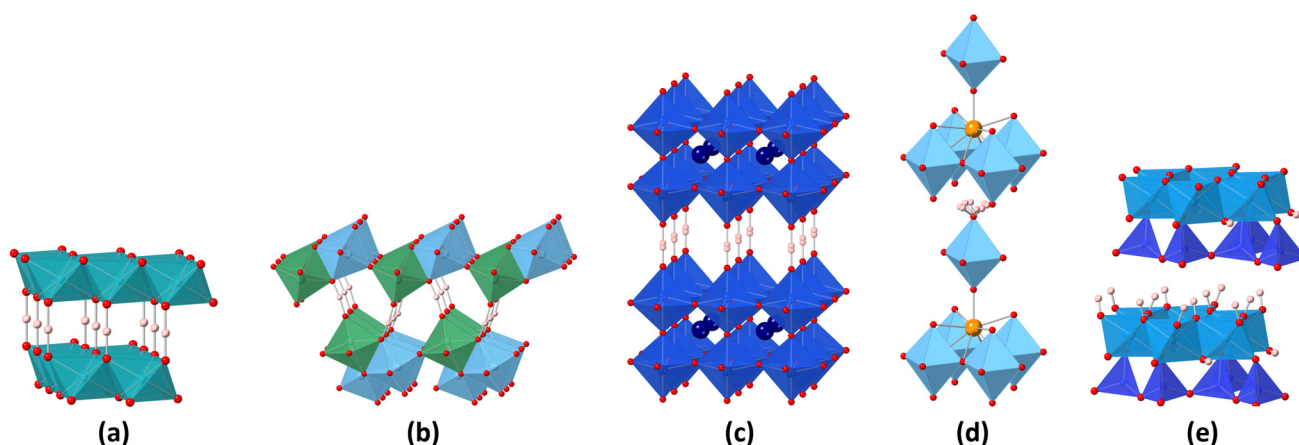


Figure 6. Comparison of the layered mixed metal oxide solid acids (a) HCoO_2 (heterogenite), (b) HTiNbO_5 , (c) HLaNb_2O_7 , (d) HNdTlO_4 (for clarity, only one H is shown on only two of the apical interlayer oxygens), and (e) $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$ (kaolinite). (Color key: Red oxygens and pink hydrogens with (a) teal cobalt octahedra, (b) green niobium and light-blue titanium octahedra, (c) blue niobium octahedra and dark-blue lanthanum, (d) blue-green titanium octahedra and amber neodymium, and (e) blue silicon tetrahedra and sky-blue aluminum octahedra).

Table 4. Comparison of bond lengths and interatomic distances for some layered mixed metal oxide solid acids.

Compound	M-O *	M	O–H	O–H...O	O...O	Reference
HCoO_2	1.897 b (x3)	Co	1.248	1.248	2.496	[56]
HTiNbO_5	2.123 b (x2) 2.114 b (x2) 1.707 a	Ti/Nb	1.185	1.335	2.515	[57]
HLaNb_2O_7	1.79 a	Nb	1.15	1.40	2.54	This work
HNdTlO_4	1.810 a	Ti	1.038	1.978	2.962	[58]
$\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$	1.906 b (x2)	Al	0.976	2.041	2.949	[59]

* b—bridging oxygens between 2 or 3 edge-sharing octahedra; a—apical oxygen.

Due to the short strong hydrogen bond formation in HLaNb_2O_7 , it would be expected that proton mobility would be minimal. Researchers have found conductivity in this compound [31,34], but it has been attributed to surface protons. Sato et al. noted a jump in conductivity above 350 °C [37]; this change, however, is expected to be influenced by the formation of $\text{LaNb}_2\text{O}_{6.5}$ from the decomposition of HLaNb_2O_7 [61].

Ion-exchangeable layered Dion–Jacobson perovskites exhibit a symmetric interlayer defined by the protruding apical oxygens of the corner-sharing octahedra. Varying the interlayer alkali metal cation (e.g., A = Li–Cs in ALaNb_2O_7) [39], the layers shift from being eclipsed for large eight-coordinate cations (Rb, Cs), to partially staggered for the intermediate six-coordinate cation (K), to staggered for the small four-coordinate cations (Li, Na). This size dependence of layer orientation highlights the structural flexibility of these compounds and the influence the interlayer species has on structure. In the case of hydrogen, the structure reverts to the eclipsed structure, but with the hydrogen occupying a two-coordinate site bridging (hydrogen bonding) between adjacent apical oxygens. This is different than the corresponding Ruddlesden–Popper-layered perovskites, as shown

for HNdTiO_4 (Figure 6d), where the solid acids typically have a staggered structure to accommodate double the number of hydrogens ($\text{H}_2[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$; A is an alkaline earth metal, rare earth, or main group element, B is a transition metal, and n is the number of octahedral layers). The likely occurrence of LBHB in HLaNb_2O_7 suggests that the Dion–Jacobson series could serve as an effective platform for fundamental studies of localized protons where compositional variation in these materials may offer further insight into this behavior and its influence on structure. Expanded studies into the known series of Dion–Jacobson solid acids $\text{H}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$, such as HLaM_2O_7 , ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$; $\text{M} = \text{Nb}, \text{Ta}$), $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, and $\text{HNa}_2\text{CaNb}_4\text{O}_{10}$, may be of interest as one can probe the influence of the mixed metal oxide layer composition, thickness, and octahedral tilting on short strong hydrogen bonds.

5. Conclusions

HLaNb_2O_7 is a key intermediate in several topotactic reactions, as well as a member of a structurally diverse set of layered compounds. Understanding the impact the proton has on this compound begins with an appreciation of its centric nature and corresponding strong hydrogen bonding. Similar behavior is expected to occur in other acid-exchanged Dion–Jacobson layered perovskites. Subsequent exploration of this series may lead to effective methods of tuning hydrogen bonding strength, possibly contributing to a better understanding of the role of hydrogens in such host structures.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/solids7050049/s1>. The supporting information file contains: Figure S1. (a) Images of free white powders of $\text{RbLaNb}_2\text{O}_7$ (left) and HLaNb_2O_7 (right). SEM images of (b) $\text{RbLaNb}_2\text{O}_7$ and (c) HLaNb_2O_7 . Figure S2. Fourier density image of HLaNb_2O_7 . Figure S3. FTIR spectra for both $\text{RbLaNb}_2\text{O}_7$ and HLaNb_2O_7 . Table S1. Raman data comparing Nb–O A_{1g} in the series ALaNb_2O_7 ($\text{A} = \text{H}, \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$). Table S2. Full unit cell geometry optimization atomic positions from PBE-SOL functional with Projector Augmented Wave (PAW) pseudo potentials. Table S3. Full unit cell geometry optimization atomic positions from PBE-SOL functional with the addition of dispersion interactions from the Grimme-D2. Ref. [39] is also cited in the Supplementary Materials.

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