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Intercalation of primary alcohols into layered titanoniobates

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ABSTRACT: Lamellar oxides form an important class of functional materials and are often susceptible to topotactic substitution of the ions between the layers. This opens up the structure to direct reactions with alkylammonium ions often substituting for group one ions forcing an increase in layer separation. Proton exchange with group one ions is also possible in mineral acids with the resulting protonated materials typically being acidic. These solid acids can further react with bases such as alkyl amines again causing an increase in interlayer separation. Alcohols do not readily form stable ROH_2^+X^- (R alkyl chain, X halide) species and being less basic than RNH_2 are less commonly investigated for intercalation into layered oxides. Here the intercalation of simple primary alcohols of the form ROH ($\text{R} = \text{C}_x\text{H}_{2x+1}$; $x = 1-10$) is investigated using the layered titanoniobate HTiNbO_5 as the ceramic host. Direct reaction is found to be ineffective so instead butylamine is first intercalated followed by reaction with the primary alcohols. The butylamine remains in the final product but intercalation of the alcohols causes a significant modification of the interlayer space of the ceramic. This shows how alcohols can be used to influence the interlayer space of oxide sheets in functional layered oxide ceramics.

Introduction

Layered compounds are investigated extensively worldwide with a view to producing new advanced materials through the intercalation of guest species into a two-dimensional host.^{1,2,3,4} A wide variety of properties can be affected by the interaction of the ceramic and intercalant. For example the loading capacity of carbon capture and storage materials⁵ and the properties of high temperature solid lubricants.⁶ Sometimes the release of the intercalant

under controlled conditions is important such as the gradual release of intercalated medicines⁷ or fertilizers.⁸ Due to interfaces scattering phonons, hybrid multilayer superlattices are of great interest for thermoelectric materials. For example thin films with ZnO / hydroquinone superlattices show a significant decrease in the thermal conductivity compared to pure ZnO films.⁹ TiS_2 is a layered compound that when hexylammonium is intercalated shows a thermal conductivity reduction of two orders of magnitude compared to pure TiS_2 .¹⁰

In addition to affecting physical properties intercalation can also influence the electronic properties. When diamines are intercalated in the semiconducting TiNiCl the material becomes superconducting with transition temperatures ranging from 6.8 to 17.1 K.¹¹ By intercalating molecular spacers in FeSe the superconducting transition temperature can be enhanced.¹² A review of intercalation in iron chalcogenide superconductors by Vivanco and Rodriguez¹³ suggests that tuning the transition temperature up to 45 K via intercalation is possible. Intercalation can affect superconductivity in other systems such as the superconducting cuprates. The high pressure synthesized $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ for example has a T_c of 126 K when dry but another superconducting phase with $T_c \approx 90$ K forms on intercalation of water.¹⁴ Water intercalates into many other materials with rock salt blocks. $\text{Sr}_3\text{Fe}_2\text{O}_7$ has two water derivatives as well as a dry form, all three exhibit different magnetic behavior.¹⁵

A further example of the versatility of layered intercalation compounds is in the field of heterogeneous photocatalysts.^{16,17} Here often the inorganic material provides the catalytic centers and the organic component is used to either as a photon collector¹⁸ or to increase the active surface area.¹⁹ Compounds of titanium oxide and niobium oxide

Figure 1 KTiNbO_5 viewed down the b axis with Ti/Nb Octahedra and K circles. The octahedra form edge shared pairs linked by corner sharing forming sheets.

are attracting significant interest due to their semiconducting nature and ability as UV catalysts.²⁰

There are many possible layered inorganic host materials such as layered double hydroxides (LDHs),²¹ Ruddlesden-Popper²² and Dion-Jacobson phases.²³ In the present work, KTiNbO_5 , described as having a lepidocrocite ($\gamma\text{-FeOOH}$)-related structure,²⁴ is investigated. The structure of the KTiNbO_5 parent structure is shown in Figure 1 where sheets of TiNbO_5^- are separated by K^+ . The sheets consist of pairs of edge shared octahedra linked via corner sharing forming zigzag strings. Each layer can be considered 'anti-parallel' with the layers above and below. The potassium ions reside in a distorted pseudo cubic environment between sheets. Similar compounds can be made with Rb^+ , Tl^+ or Cs^+ but Na^+ and Li^+ cause the TiNbO_5^- layers to adopt a 'parallel' configuration.^{25,26} These monovalent ions can be exchanged out for protons²⁷ before further reaction with n-alkyl amines. Further reaction allows large molecules such as methylene blue,²⁸ Rhodamine 6G,²⁹ porphyrin^{30,31} and polymers such as polyaniline³² to then be incorporated.

Intercalation of n-alkyl alcohols has so far been overlooked as direct reaction appears unsuccessful. In addition HTiNbO_5 is a solid acid catalyst that has been shown to dehydrate secondary alcohols.^{33,34} It is this acidity that allows intercalation of the basic amines (amines with $\text{pK}_a > 6$)³⁵ using a proton donation mechanism. Primary alcohols are less basic than primary amines explaining the lack of reaction of n-alkyl alcohols. Competition reactions using lower alcohols, amines and HTiNbO_5 also appear to be unsuccessful. Previous work by Rebbah et al²⁷ found using a 50 % alcohol to amine solution could be used instead of neat amine 'without changing the results'.

Alcohols, however, have been grafted into the interlayer space of the $n = 3$ Ruddlesden-Popper phase $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ with Ti-O-C bonds being formed.²² The process goes through an amine intercalate intermediate, again formed via acid base reaction giving RNH_3^+ ions at the proton sites. The reaction with alcohols appears to graft the alkyl part of the alcohol to the metal oxygen octahedra, the hydroxide and proton form water freeing the amine.

In this paper we show the intercalation of primary alcohols of carbon chain length 1 -10 between the $(\text{TiNbO}_5)^-$ layers of $(\text{RNH}_3)^+ (\text{TiNbO}_5)^-$ intermediates.

Experimental

Synthesis

KTiNbO_5 was first synthesized by grinding stoichiometric amounts of K_2CO_3 (Alfa Aesar, 99.0%), TiO_2 (Alfa Aesar, 99.5 %) and Nb_2O_5 (Alfa Aesar, 99.95 %) together, pressing into 13 mm pellets and firing in air at 1100 °C for 12 hours. Then the material was ground and soaked in 2M HCl (Alfa Aesar 32% diluted with distilled water) for 12 hours, before being filtered and washed with distilled water to remove excess acid and KCl. The powder was then dried in a fumehood giving HTiNbO_5 . The resulting white powder was then heated to 70 °C in a sealed vessel (Teflon

lined Parr autoclave) with excess butylamine (Sigma-Aldrich > 99%). The conditions used were not solvothermal rather used as a convenient way to contain fumes.

After filtering and drying in a fumehood the $(\text{Bu}_4\text{NH}_2)_x\text{HTiNbO}_5$ was then heated to 70 °C in a sealed vessel (Teflon lined Parr autoclave) with excess neat primary alcohols methanol (CH_3OH) to decanol ($\text{C}_{10}\text{H}_{21}\text{OH}$) (all > 98%). Resulting white powders were filtered and again dried in a fumehood.

Characterization

Figure 2 XRD patterns for a) original ceramic (KTiNbO_5), b) Proton exchanged ceramic (HTiNbO_5), c) amine intercalated $((\text{butylNH}_2)_x\text{HTiNbO}_5)$ and d) –g) alcohol intercalated $((\text{butylNH}_2)_x(\text{ROH})_y\text{HTiNbO}_5$ where d) methanol e) butanol f) hexanol and g) decanol. Significant Miller indices in *italics* for a) and b) and **bold** for c)–g)

Powder X-ray diffraction (XRD) was carried out on a monochromated Cu source ($\text{K}\alpha_1$, $\lambda = 1.54056 \text{ \AA}$) PANalytical X'Pert Pro diffractometer operated at 45 kV 40 mA. Le Bail³⁶ and Rietveld³⁷ analysis was carried out using the General Structure Analysis System (GSAS) suite of programs³⁸ with the EXPGUI³⁹ user interface.

Thermogravimetric analysis (TGA) data were recorded on a Perkin Elmer Pyris thermal balance with a high temperature furnace using a 40 ml min^{-1} nitrogen gas stream. During the heating cycle the temperature was increased at a rate of 1 °C per minute to 1000 °C. The cooling was either carried out radiatively to 300 °C upon which the furnace detached exposing samples to air (denoted radiatively cooled) or at 1 °C per minute to 30 °C (denoted slow cool).

Fourier transform infrared spectroscopy (FTIR) was carried using a Nicolet PROTÉGÉ 460 spectrometer measurement range 500 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1} . The measurement was carried out in transmission mode using 13 mm diameter KBr disks containing 200 mg of dried KBr and 1 mg of sample.

Carbon hydrogen and nitrogen (CHN) analysis was carried out using a Perkin Elmer CHNS/O 2400 series II.

Results

Primary alkyl alcohols with chain lengths of between 1 and 10 have successfully been intercalated between titanoniobate sheets. All samples are white crystalline powders making X-ray diffraction the primary method of analysis.

Powder X-ray diffraction results

The crystal structure of the parent KTiNbO_5 was described by Wadsley in 1964.⁴⁰ Wadsley reported the Ti and Nb being present at random in two positions. However diffuse streaks were ascribed to 'short range order accompanying the random distribution'. Latter x-ray diffraction and neutron diffraction work by Rebbah *et al.*^{25,41} on both KTiNbO_5 and DTiNbO_5 reports 0.77:0.23 site selectivity. Sugimoto *et al.*⁴² also report site selectivity of 0.80(1):0.20(1).

Rietveld refinement of the original KTiNbO_5 gives lattice parameters (Pnma, $a = 6.44288(3) \text{ \AA}$, $b = 3.79635(2) \text{ \AA}$, $c = 18.3851(1) \text{ \AA}$ in agreement with Wadsley⁴⁰ (Pnma $a = 6.46 \text{ \AA}$, $b = 3.79 \text{ \AA}$, $c = 18.47 \text{ \AA}$). The Rebbah^{41,43} model of preferential order of Ti and Nb in DTiNbO_5 was used as starting point giving values of 0.781(3):0.220(3) (supplementary data S1-3).

All PXRD patterns can be indexed to orthorhombic cells consistent with space group Pnma (KTiNbO_5 , HTiNbO_5 , $(\text{ButylNH}_2)_x\text{HTiNbO}_5$, $(\text{ButylNH}_2)_x(\text{C}_2\text{H}_5\text{OH})_y\text{HTiNbO}_5$, $(\text{ButylNH}_2)_x(\text{C}_{10}\text{H}_{21}\text{OH})_y\text{HTiNbO}_5$ shown in figure 2 all other samples supplementary figure S5. As proton positions cannot be refined using X-ray radiation, Le Bail refinement was carried out to determine the lattice parameters for the HTiNbO_5 unit cell ($a = 6.5279(5) \text{ \AA}$, $b = 3.7740(2) \text{ \AA}$, $c = 16.704(3) \text{ \AA}$). Le Bail refinements were also performed for all of the intercalated samples with the lattice parameters given in the supplementary table S4. As expected as the size of the intercalated molecule gets larger the c parameter increases but a and b parameters remain constant ($a \approx 6.47(2) \text{ \AA}$, $b \approx 3.795(10) \text{ \AA}$).

Figure 3 FTIR results: a) HTiNbO_5 b) $(\text{butylNH}_2)_x\text{HTiNbO}_5$ c) $(\text{butylNH}_2)_x(\text{C}_4\text{H}_9\text{OH})_y\text{HTiNbO}_5$ and d) $(\text{butylNH}_2)_x(\text{C}_{10}\text{H}_{21}\text{OH})_y\text{HTiNbO}_5$. Y axis offset by multiples of 100 to prevent data overlap. Detailed description in main text

Fourier transform infrared spectroscopy

All samples were examined using FTIR (figure 3 and figure S6) with a clear difference between the HTiNbO_5 and the intercalated samples being observed. The cluster of bands at ≈ 900 , 630 and 515 cm^{-1} were identified by Lambert *et al.*⁴⁴ as originating from the octahedral modes of TiO_6 and NbO_6 . M-O-H bending modes also identified by Lambert are seen at 946 , 978 and 1080 cm^{-1} . For HTiNbO_5 the broad band at $\approx 2700 \text{ cm}^{-1}$ shows strong O-H...O hydrogen bonding between TiNbO_5^- sheets and small band at 1610 cm^{-1} from H bonded H_2O . When amines and alcohols are intercalated these H bonds are broken so the O-H stretch shifts to higher wavenumbers. The O-H and N-H now overlap causing the extremely broad band centered at $\approx 3000 \text{ cm}^{-1}$ observed for the intercalated samples.

In addition to these bands there is a triple peak characteristic of C-H stretches. The C-H and N-H bends appear at $\approx 1500 \text{ cm}^{-1}$. As the spectra for amine intercalated and alcohol intercalated materials are similar FTIR cannot discriminate between intercalated species.

Thermogravimetric analysis data

In addition to FTIR, TGA was carried out (Figures 4 and S7) with post-TGA XRD being used to assign final products. Analysis of these post-TGA XRD patterns showed that when cooled radiatively sample showed mixture of TiO_2 and Nb_2O_5 . Slow cooled samples however showed either $\text{Ti}_2\text{Nb}_2\text{O}_9$ phase or TiNbO_4 (rutile form). The determining factor appears to be the drop at approximately 800°C . If this drop is present with no recovery TiNbO_4 is the final product. If some weight is recovered due to oxidation, $\text{Ti}_2\text{Nb}_2\text{O}_9$ becomes the final product. The $\text{Ti}_2\text{Nb}_2\text{O}_9$ phase is a well-known dehydration phase of HTiNbO_5 .⁴⁵ Structurally the metal octahedra remain but the interlayer hydrogen bonds are replaced by corner sharing of octahedra between layers. Visually the TiNbO_4 appears dark blue to black, characteristic of Nb^{4+} while $\text{Ti}_2\text{Nb}_2\text{O}_9$ samples appear white. Reported synthesis conditions for TiNbO_4 are

Figure 4 TGA results: a) KTiNbO_5 b) HTiNbO_5 c) $(\text{butylNH}_2)_x(\text{C}_4\text{H}_9\text{OH})_y\text{HTiNbO}_5$ d) $(\text{butylNH}_2)_x\text{HTiNbO}_5$ and e) $(\text{butylNH}_2)_x(\text{C}_{10}\text{H}_{21}\text{OH})_y\text{HTiNbO}_5$

NbO₂ and TiO₂ heated to 650 °C, then 950 °C in an evacuated quartz tube.⁴⁶ As the length of the carbon chain of the alcohol increases the initial (sub 100 °C) weight loss ascribed to surface water also increases.

The powders also change in their tactile behavior going from dry brittle ceramic at low carbon content to soft almost polymer powder at higher carbon contents. Above 100 °C interlayer water is lost before the organics begin to de-intercalate.

Comparing the intercalated phases to the parent HTiNbO₅ the weight loss gradient change at approximately 230 °C is the loss of the proton as ½ H₂O. For butylamine and lower alcohols this is almost a separate transition but for the higher alcohols merges into general weight loss. Overall after loss of surface water the process is shown in Figure 5.

Figure 5 Weight loss steps after surface water loss

The last step which Chausson et al⁴⁷ asserts is remaining surface ammonium that leaves above 800 °C. This does not occur for HTiNbO₅ as there is no ammonium to begin with. When the ammonium has completely left by around 900 °C the powder has been reduced to TiNbO₄. As the amount of intercalated amine (x) is approximately 0.5 the equation for this process becomes;

Elemental analysis results

As the temperature ranges where butylamine and the alcohols de-intercalate overlap TGA alone is unable to resolve relative amounts of amine and alcohol. CHN analysis was therefore carried out with the results given in Table 1. The molecular masses obtained from CHN and TGA show good agreement.

Kikkawa and Koizumi⁴⁸ have argued on the basis of space arguments that the material is only able to accommodate ½ mole of butylamine per mole of HTiNbO₅. From table 1 the amount of butylamine incorporated is 0.66 moles per mole of ceramic comparable to the 0.66 moles propylammonium to 1 mole TiNbO₅ of Nakato et al.⁴⁹

Table 1 Elemental composition from CHN for (butylNH₂)_x(ROH)_yHTiNbO₅ with calculated mass (RMM CHN) compared to calculated mass from TGA(RMM TGA)

Carbons per Alcohol	Moles butylamine (x)	Moles Alcohol (y)	RMM CHN	RMM TGA
Butylamine	0.66(1)	0	269.3(3)	269.2(5)
1	0.528(4)	0.24(5)	264(1)	264(1)
2	0.529(7)	0.11(3)	263.5(5)	263.3(7)
3	0.535(8)	0.08(1)	264.0(5)	269(1)
4	0.510(4)	0.09(1)	264.50(5)	266(1)
5	0.540(7)	0.10(1)	268.50(5)	267(3)
6	0.517(6)	0.13(1)	271(1)	274.6(7)
7	0.506(7)	0.206(9)	279.0(5)	277(2)
8	0.52(8)	0.254(8)	288.50(5)	294(1)
9	0.464(7)	0.30(1)	294.0(5)	292(2)
10	0.475(7)	0.310(8)	300(1)	303(6)

Some excess amine is therefore able to pack with the intercalated amine. Washing procedures vary between reports with both Kikkawa⁴⁸ and Nakato⁴⁹ using acetone while Rebbah²⁷ uses alcohol and in this report samples are not washed but dried. Lambert et al⁴⁴ noticed a change in interlayer spacing (c/2) depending on whether samples were washed or not for their alkylammonium materials. For the butyl-ammonium case 20.37(6) Å unwashed versus 18.03 Å washed or 17.67 Å when butylamine was used instead of butyl-ammonium chloride. Lambert proposed this was due to 'the occurrence of excess intercalation' which could be washed out. In this report when (butylNH₂)_xHTiNbO₅ is subsequently subjected to alcohol treatment the intercalated amount of butylamine drops to approximately 0.53. This value is considerably closer to Lambert's ideal value of 0.55 and Kikkawa's 0.5. Thus approximately 0.5 butylamine binds in the accepted acid base fashion to the ceramic layers with the remaining 0.16 packing in an alkyl chain to alkyl chain fashion (excess intercalation). When the alcohol is introduced the packed butylamine is displaced leaving the alcohol now packed. A possible driving force for this could be the OH⁻ group being better able to hydrogen bond with the remaining free proton on the opposing ceramic sheet. Or it could simply be a steric issue as the alcohol head group will be smaller than the corresponding amine group. As alcohol chain length increases the relative amount of butylamine decreases meaning the intercalation of larger chain alcohols is more favorable.

Discussion

The method of alcohol insertion is described in this report as intercalation rather than grafting^{19,22,50} or dissociative absorption³³ as no M-O-C bonds are formed. This distinction was used by Tahara et al²² for amine intercalation and alcohol grafting in $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$. In systems where grafting occurs the ceramic layer is often based on perovskite derivatives such as the Ruddlesden-Popper $\text{H}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ ²² or the Triple-Layered $\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}\cdot x\text{H}_2\text{O}$.⁵⁰ An important structural difference between these perovskite derivatives and HTiNbO_5 can be found in how the metal oxide octahedra are connected. In perovskite all octahedra are corner shared where in HTiNbO_5 there are edge shared pairs (Figure 1). This significantly alters the interlayer space allowing easier access to the interlayer gallery for perovskite derivatives. The straight gallery contrasts with the kinked gallery in HTiNbO_5 . In some cases such as $\text{H}\text{Ca}_2\text{Nb}_3\text{O}_{10}$ ⁵⁰ and $\text{H}\text{LaNb}_2\text{O}_7$,⁵¹ this increased access coupled with increased acidity of pure Nb-O sheets³³ allows direct hydrolysis-esterification reactions. These reactions are required to graft alcohols to ceramics. In HTiNbO_5 however amines must first be intercalated to push apart the layers to allow intercalation of alcohols.

A common way to describe the effect of intercalation of amines is to look at a plot of interlayer space versus carbon chain length.^{27,44,48,52} In Figure 6, we show a similar plot for the present alcohol intercalation system using the model described in the previous section. Using this model two regions would be expected. First a plateau with interlayer spacing = butylamine interlayer spacing until the packed alcohol becomes larger than the butylamine. Then when the alcohol becomes larger than the butylamine the interlayer space increases in a linear fashion with a gradient similar to that observed for amines. Two regions are seen in the data. The lattice parameters for lower alcohols (filled squares figure 6) are indeed very similar to butylamine intercalate however the CHN analysis and the TGA show alcohol is being included.

For the present system the transition between the two regions occurs around 6 carbons not the expected 4. For comparison the expected value of plateau is shown by a dashed line and literature data for aliphatic primary amines are also given in Figure 6. Using linear fits the increase in interlayer space below hexanol can be fitted to $0.34(3)X+16.7(1)$ and above hexanol to $1.7(2)X+8.7(13)$. The gradient of the above hexanol region is comparable (within error) with the average gradient of aliphatic amines $1.97(8)$. The intercept values correspond to the c parameter for HTiNbO_5 below hexanol while above hexanol the interlayer space ($c/2$) value for HTiNbO_5 of $8.3 \text{ \AA}$ is seen. If the lower alcohols had no effect on the butylamine then the intercept would be that of $(\text{butylNH}_2)_x\text{HTiNbO}_5$ ($18.29 \text{ \AA}$) and gradient would be 0 (rather than $0.34(3)$). This shows the effect that the alcohol has on the amine intercalation angle, as alcohol size decreases tilt angle increases. Taking this to the extreme when there are no carbons and a tilt angle of $\approx 90^\circ$ butylamine would be along ab plane. As there will be butylamine on both sides of the interlayer a C-H bond from each side has to be accommodated in a

Figure 6 Interlayer distances ($c/2$) plotted against number of carbons in the alkyl chain. Filled squares/triangles are alcohol intercalated samples with solid lines being the linear fits described in main text. Empty squares are reference data^{27,48,52} for amine only intercalation with a dotted line fit. Dashed line interlayer spacing of butylamine intercalated material (this report).

(C-H H-C) fashion. This is in contrast to the experimental structure of HTiNbO_5 where the proton links the sheets in a O-H---O fashion. The result of this is a theoretical doubling of the interlayer space for $C=0$ versus experimental HTiNbO_5 ((C-H H-C) vs (O-H---O)). As interlayer space is $c/2$ the intercept value for $C=0$ is the c parameter for HTiNbO_5 . As for the higher alcohols, increase in interlayer space is only due to alcohols increasing chain length then extrapolating back to no alcohol gives value of original non-intercalated ceramic HTiNbO_5 . The amine intercept of $10.1(5) \text{ \AA}$ is close to the $9.51 \text{ \AA}$ reported for $\text{NH}_4\text{TiNbO}_5$ ($C=0$ amine).⁴⁸

Amines are widely reported to intercalate at angles less than 90° for HTiNbO_5 when taking the c axis as being the vertical. Also as referred to previously only 50% of the possible proton binding sites are filled. When low chain alcohol gets in between these bound butylamine molecules it forces them to pack and tilt away from the c axis. The result of this is that instead of a plateau of interlayer space equal to $(\text{butylNH}_2)_x\text{HTiNbO}_5$ a linear increase is observed. This increase continues past butanol to hexanol meaning this tilting creates extra space. Interlayer space (c parameters) for butanol and butylamine are similar but pentanol and hexanol are significantly reduced compared to their amine counterparts. A decrease in the tilt angle away from c axis was reported by Shangguan and Yoshida⁵³ as the chain length of intercalated amine increases. Past hexanol the gradient changes drastically meaning past this point the alcohol on both sides is contributing to the packing and addition of an extra CH_2 group now requires full expansion of space rather than altering the intercalation angle.

Figure 7 Schematic picture of the arrangement of the butylamine (left) based on Lambert's figure 6b⁴⁴ and lower alcohols (middle) and higher alcohols (right) intercalates between the Ti/Nb oxide layers. For clarity the hydrogens have been omitted.

Schematically this is shown in Figure 7: first the butylamine intercalation, second the low alcohol causing amine intercalation angle to change. The angle away from *c* increases from a minimum at hexanol to maximum at methanol with the angle for butanol being similar to the angle for pure butylamine. Above hexanol the increase in interlayer space is predominantly caused by the alcohol chains coming in contact across the space rather than a change in angle (final panel of Figure 7). Experimentally this change in cause of interlayer increase is seen by the gradient change in Figure 6. Above hexanol gradient becomes similar to that of the pure amines where although tilting is present the increase is caused by increasing chain length (similar to Lambert's model 6b).⁴⁴

Conclusions

Inorganic/organic hybrids of the form $(\text{RNH}_2)_x(\text{ROH})_y\text{HTiNbO}_5$ have been synthesized and characterized by X-ray diffraction, thermogravimetric analysis and CHN analysis. The alcohols intercalate into $(\text{butylNH}_2)_x\text{HTiNbO}_5$ rather than graft as observed previously in Ruddlesden-Popper phases. The amine is key to allowing alcohols into the structure. This anchoring behavior could be used to the synthetic chemists' advantage as any molecule with a primary alcohol side chain becomes a candidate for intercalation. The multistep method described in this report to intercalate alcohol in $(\text{TiNbO}_5)^-$ systems could be expanded to other layered systems. Any layered system where amines can intercalate such as TiS_2 , TiNCl and FeSe could also intercalate alcohol in a manner similar to HTiNbO_5 . The vast range of layered materials and molecules with a primary alcohol side chain opens up significant opportunities for new functional organic-ceramic hybrids.

ASSOCIATED CONTENT

Supporting Information consists of Rietveld information for KTiNbO_5 , lattice constants for $(\text{butylNH}_2)_x(\text{ROH})_y\text{HTiNbO}_5$, XRD patterns FTIR and TGA data.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Primary alcohols have been intercalated between the layers of HTiNbO₅ for the first time via a two-step process. As alcohols are less basic than amines they are unable to go via the one step acid base mechanism instead requiring an amine intermediate. Intercalation causes a significant expansion of the unit cell followed by XRD. This shows how alcohols can be used to influence the interlayer space of oxide sheets in functional layered oxide ceramics.