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Synthesis of $H_xLi_{1-x}LaTiO_4$ from Quantitative Solid State Reactions at Room Temperature

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The layered perovskite $HLaTiO_4$ reacts stoichiometrically with $LiOH \cdot H_2O$ at room temperature give targeted compositions in the series $H_xLi_{1-x}LaTiO_4$. Remarkably, the Li^+ and H^+ ions are quantitatively exchanged in the solid state and this allows stoichiometric control of ion exchange for the first time in this important series of compounds.

The development of a number of important technologies, including batteries and fuel cells, relies on the discovery of new materials capable of ionic conductivity under chemically and thermally demanding conditions. The synthesis of such solids is typically carried out at high temperatures that access only the most thermodynamically stable phases. It is now appreciated that it is possible to manipulate the products of these high temperature reactions at reduced temperature and break selected bonds and this has lead to the formation of a range of unusual compounds.¹⁻³

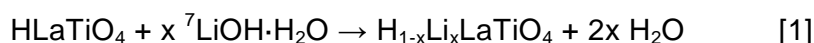
A number of low temperature modifications have been performed on a family of layered compounds related to the perovskite structure. These Ruddlesden Popper (RP) phases consist of a variable thickness of perovskite separated by a layer of rock salt structure. The RP compound $NaLaTiO_4$ consists of a single layer of corner sharing TiO_6 octahedra separated by an unusual arrangement of alternating layers of Na^+ and La^{3+} cations. The Na^+ can be replaced by other monovalent cations by treating this material with an aqueous solution containing an excess of an appropriate salt, such as $LiCl$ to yield $LiLaTiO_4$, or acid, such as HNO_3 to give $HLaTiO_4$ or treatment with a molten salt at elevated temperature.⁴ In all cases the ion exchange is driven by the cation excess and proceeds over several hours or days often at elevated temperature, either by reflux in the case of aqueous solutions, or else above the melting point of the salt. These conditions provide no control over the degree of exchange and consequently the product is usually the fully exchanged material.

We have recently shown how a spontaneous reaction at room temperature between two solids, $LiOH \cdot H_2O$ and MoO_3 , is entropically driven by the liberation of water of crystallisation that occurs on the formation of Li_2MoO_4 .⁵ The particle morphology of the product indicates that the reaction proceeds via partial dissolution in the water of crystallisation and subsequent particle growth. Here, we exploit this entropic driver to obtain an ion exchange reaction in the RP structure at room temperature. Remarkably,

the Li⁺ and H⁺ ions are quantitatively exchanged in the solid state whilst retaining particle morphology and crystallinity and so this demonstrates a fundamentally new reaction that exploits room temperature ionic conduction. This allows stoichiometric control of ion exchange for the first time in this important series of compounds. Moreover, this methodology should be generally applicable to the large number of related proton-containing RP phases and so may provide access to a library of new compounds.

NaLaTiO₄ was prepared via high temperature synthesis⁶ from appropriate oxides and carbonates and treated with nitric acid⁷ to give HLaTiO₄. This solid acid was reacted with one equivalent of hydrated lithium hydroxide, LiOH·H₂O, by grinding at room temperature for 30 min. The powder mixture became less friable with grinding but did not become tacky or damp, despite the reaction generating two molar equivalents of water. X-ray powder diffraction data collected immediately after grinding showed that the basic structure of the Ruddlesden Popper phase had been retained and that the lattice parameters had undergone a substantial contraction to the values expected for LiLaTiO₄.⁸ Scanning electron micrographs show that this material has the same monolithic particle morphology as the HLaTiO₄ reagent and the NaLaTiO₄ precursor suggesting that Li⁺ had been exchanged for H⁺ without the dissolution or delamination of the perovskite layers that can occur in ion exchange.⁹

The process was repeated using a reduced ratio of LiOH·H₂O to carry out the reactions [1]:



This afforded a series of compounds that exhibited X-ray powder diffraction patterns that could be indexed using the same space group, P4/nmm, as HLaTiO₄ and LiLaTiO₄, but with a smooth evolution in lattice parameters between these compounds as shown in Figure 2. There was some reduction in crystallinity as shown by a ca. 70 % increase in the peak width but the data were still amenable to structural analysis.

Neutron diffraction data were collected from H_{0.5}Li_{0.5}LaTiO₄ at room temperature using the constant wavelength diffractometer D2B at the Institute Laue Langevin in Grenoble. The data were fitted in the space group P4/nmm with a mixture of H⁺ and Li⁺ in the interlayer galleries. The position of the hydrogen atom was fixed at coordinates derived from full refinement against neutron diffraction data collected from HLaTiO₄.¹⁰ The H/Li content was refined freely within the constraints of charge balance to the composition H_{0.46(2)}Li_{0.54(2)}LaTiO₄ that gave excellent agreement with the target stoichiometry. The final refinement constrained the composition to that of the reaction mixture to give the fit

shown in Figure 3. The H⁺ and Li⁺ cations are disordered in the interlayer space; the proton is disordered over eight positions around each of the apical oxide anions at a short distance, 1.03 Å, that is typical for protonated oxide.¹¹ The lithium cations are coordinated to four oxide anions at 2.0131(13) Å with a O-Li-O angle, 97.6°, that is intermediate between tetrahedral and square planar geometries.

The peak widths of this phase show that the crystallinity is largely unaffected by the presence of a mixture of H⁺ and Li⁺ in the interlayer space in H_{0.5}Li_{0.5}LaTiO₄. Transmission electron microscope images of the sample support this observation and show no evidence for staged cation exchange. As shown in Figure 3 H_{0.5}Li_{0.5}LaTiO₄ shows lattice fringes extending over > 10 nm indicating that this sample retains considerable crystallinity.

It is known that heating HLaTiO₄ can lead to decomposition and dehydration to give an amorphous phase.¹² Thermogravimetric measurements show that H_{0.5}Li_{0.5}LaTiO₄ undergoes a large mass loss between 120 °C and 600 °C. Heating the series H_{1-x}Li_xLaTiO₄ gives a trend in mass loss that indicates that the dehydration reaction [2] is occurring.



X-ray diffraction patterns collected from the dehydrated product obtained by heating the x = 0.5 compound to 480 °C, with the nominal composition Li_{0.5}LaTiO_{3.75}, show that some crystallinity is retained. These data can be indexed using a tetragonal cell with the substantial reduction in the interlayer distance that is anticipated to result from loss of interlayer protons and apical oxide anions. Although the structure of this phase is not known, it contains a mixture of Li⁺ and vacant sites that has strong similarities with the fast Li⁺ conducting perovskites Li_{3x}La_{2/3-x}TiO₃.^{13, 14}

Figure 4 shows preliminary analysis of the transport properties of Li_{0.5}LaTiO_{3.75} with a total conductivity of 7.9(8)×10⁻⁸ S cm⁻¹ at 440 °C and an activation energy of 0.79(10) eV that are similar to those reported for the LiLaTiO₄ end member.⁸ Although this conductivity is orders of magnitude less than the perovskites, it may be that the grain boundaries are providing the limit to ion mobility.

To conclude, a direct solid-state reaction at room temperature has produced a new series of compounds. The reaction occurs without dissolution and the only side-product of the reaction is water and so no purification, other than drying in air, is necessary. Given the wide-ranging stoichiometries and structure types observed for the protonated layered perovskite phases it is probable that this reaction will open up a huge range of new compositions that are inaccessible via existing synthetic routes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedures, diffraction patterns, thermogravimetric data and electron microscopy images are available]. See DOI: 10.1039/b000000x

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Figure Captions

Fig.1 The crystal structures of the layered perovskite phases NaLaTiO₄, HLaTiO₄ and LiLaTiO₄. TiO₆ units are represented by red octahedra while black, orange, grey and yellow spheres represent La³⁺, Na⁺, H⁺ and Li⁺ respectively.

Fig. 2 The lattice parameters and unit cell volume as a function of lithium content for the series H_{1-x}Li_xLaTiO₄ derived from X-ray powder diffraction data. The estimated standard deviations are smaller than the symbol size. Empty circles and squares represent data from repeating the reaction using a different sample of HLaTiO₄ reagent. The solid black squares indicate literature values.^[7]

Fig. 3 The neutron powder diffraction profile collected from H_{0.5}Li_{0.5}LaTiO₄ at room temperature at a wavelength, $\lambda = 1.54 \text{ \AA}$. The observed data are shown as dots and the calculated pattern is shown as a solid line. Allowed Bragg peaks are indicated by vertical bars. The inset shows the lattice fringes extending over > 10 nm observed using transmission electron microscopy.

Fig. 4 The total conductivity of a sample of H_{0.5}Li_{0.5}LaTiO₄ after heating above the dehydration temperature to give a compound of nominal stoichiometry Li_{0.5}LaTiO_{3.75}. The conductivity was derived from fitting AC impedance data as shown in the inset for data collected at 440 °C using the equivalent circuit shown.