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$HNbO_3$ and $HTaO_3$: New Cubic Perovskites Prepared from $LiNbO_3$ and $LiTaO_3$ via Ion Exchange

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The synthesis of $HNbO_3$ and $HTaO_3$ from $LiNbO_3$ and $LiTaO_3$ via ion exchange in hot aqueous acid solutions is reported. This reaction is accompanied by a topotactic structural transformation from the rhombohedral $LiNbO_3$ structure to the cubic perovskite structure; cell constants are $a = 3.822(1)$ Å for $HNbO_3$ and 3.810(2) Å for $HTaO_3$. These new compounds have been characterized by powder X-ray diffraction, thermogravimetric analysis, and solid-state NMR. They are electronic insulators and have low ionic conductivity. Evidence of partially proton-exchanged phases $Li_{1-x}H_xMO_3$ was also seen. The possible significance of this ion exchange reaction for devices using $LiNbO_3$ or $LiTaO_3$ is discussed.

Introduction

$LiNbO_3$ and $LiTaO_3$ are ferroelectric and nonlinear optical materials of considerable importance for a variety of applications, including surface acoustic wave and integrated optics technologies. Although their physical properties have been extensively studied, the chemistry of these compounds at low temperatures has received very little attention. We wish to report the discovery of a rather unusual ion exchange reaction undergone by $LiNbO_3$ and $LiTaO_3$ in aqueous acid solutions. Using this reaction we have prepared $HNbO_3$ and $HTaO_3$, two previously unknown crystalline hydrous oxides having the cubic perovskite structure.

A number of researchers have studied the effects of hydrogen introduced into $LiNbO_3$ and $LiTaO_3$ crystals by treatment with water vapor at elevated temperatures (*1*). However, these studies involved crystals with far lower hydrogen concentrations than we have achieved. The ion exchange process we have discovered involves replacement of some or all of the Li^+ in these compounds with H^+, causes no reduction or color change, and is accompanied by a dramatic structure change from rhombohedral to cubic symmetry.

This topotactic structural transformation is particularly interesting because it involves exactly the same deformation of the transition metal oxide network initially proposed by Megaw (*2*) (though later shown to be incorrect (*3*)) to account for the ferroelectric transition in $LiNbO_3$. The topology of this structure change has been discussed in several papers (*2, 4–6*), but generally it has been considered to be theoretically possible but physically unlikely (*7, 8*). This ion exchange reaction of $LiNbO_3$ and $LiTaO_3$, along with recent reports of similar transitions in ReO_3 (*9, 10*) and $ZrFeF_6$ (*11*), suggests that the $LiNbO_3$ to perovskite trans-

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formation is a more facile process than was previously supposed.

In this paper we describe the synthesis and characterization of $HNbO_3$ and $HTaO_3$, and discuss some possible implications of this ion exchange reaction for devices using $LiNbO_3$ and $LiTaO_3$.

Synthesis and Characterization

Preparation of $HNbO_3$. $LiNbO_3$ powder was stirred in 8 *M* nitric acid at 95–100°C for 3 days. Samples of powder were withdrawn and an X-ray diffraction pattern was measured at 12-hr intervals during the reaction. After 3 days the mixture was filtered and the powder was washed with distilled water and air dried. The filtrate gave a strong positive flame test for lithium. The product was a dense white powder which, when heated at 800°C overnight, dehydrated to form H–Nb_2O_5. The water content of the product was determined gravimetrically: weight loss on heating was 6.09%, corresponding to a formula of $Nb_2O_5 \cdot 0.96H_2O$.

Ion exchange was found to occur in a variety of other strong acid solutions as well. The reaction time did not depend on the acid used, but was dependent on initial particle size, acid concentration, and temperature. For example, complete reaction required only 8 hr in 9 *M* H_2SO_4 at 125°C.

The preparation of $HTaO_3$ was identical to that for $HNbO_3$ except that 3 weeks were required for full reaction in 8 *M* nitric acid at 95°C. Weight loss on dehydration was 3.80%, corresponding to $Ta_2O_5 \cdot 0.97H_2O$.

X-Ray diffraction powder patterns were measured for $HNbO_3$ and $HTaO_3$ on a diffractometer using Cu$K\alpha$ radiation. Silicon was used as an internal standard. The patterns were indexed in the cubic system, and cell constants were calculated using reflections with 2θ greater than 70° to be a = 3.822(1) Å for $HNbO_3$ and 3.810(2) Å for $HTaO_3$. Diffracted intensities and interplanar spacings are listed in Table I.

Figure 1 shows line graphs of the powder patterns of pure $LiNbO_3$, and $LiNbO_3$ reacted with hot nitric acid for 1, 2, and 3 days (pure $HNbO_3$). After ion exchange for 1 day (Fig. 1b), the diffraction peaks for $LiNbO_3$ shift and broaden. Calculation of hexagonal cell constants from the shifted peaks gives a = 5.159(3) and c = 13.874(3) Å, corresponding to an expansion of 0.2% along a and 0.09% along c compared with pure $LiNbO_3$ (a = 5.1494, c = 13.8620 Å (*12*)). A number of small, broad new peaks are also visible. After 2 days of reaction, the diffraction lines of cubic $HNbO_3$ dominate the pattern, while the $LiNbO_3$ peaks have receded; note, however, that there are a few small peaks which are intermediate between the lines of $LiNbO_3$ and $HNbO_3$ and belong to neither set; these extra lines are marked by arrows in Fig. 1. After 3 days of reaction, the only lines visible are those of cubic perovskite $HNbO_3$.

TABLE I

X-RAY DIFFRACTION PATTERNS FOR $HNbO_3$ AND $HTaO_3$

	$HNbO_3$		$HTaO_3$	
h k l	*d* (Å)	*I*	*d* (Å)	*I*
1 0 0	3.832	100	3.805	100
1 1 0	2.708	45	2.697	50
1 1 1	2.209	8	2.200	15
2 0 0	1.914	15	1.905	12
2 1 0	1.710	30	1.704	30
2 1 1	1.562	15	1.556	15
2 2 0	1.352	5	1.348	4
2 2 1, 3 0 0	1.275	8	1.270	8
3 1 0	1.208	4	1.204	3
3 1 1	1.153	4	1.149	3
3 2 0	1.060	2	1.056	1
3 2 1	1.0214	4	1.0184	4
3 2 2, 4 1 0	0.9269	3	0.9242	3
3 3 0	0.9008	3	0.8986	3
3 3 1	0.8769	1	0.8740	1
4 2 1	0.8339	2	—	—
3 3 2	0.8148	1	—	—

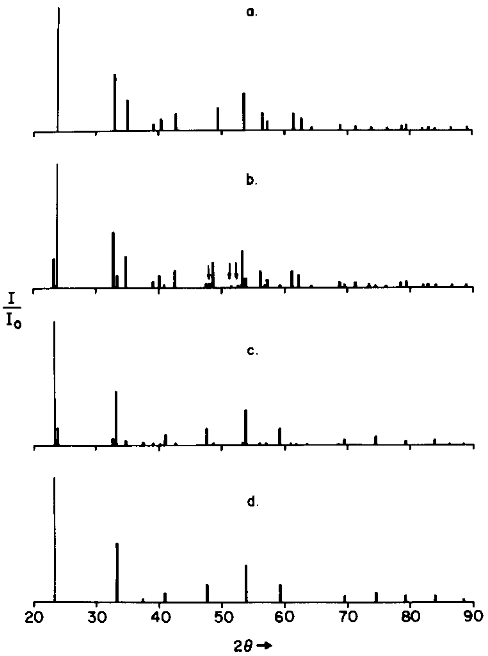

FIG. 1. Line graphs of X-ray powder diffraction patterns recorded during the $LiNbO_3$ to $HNbO_3$ reaction. (a) $LiNbO_3$; (b) $LiNbO_3$ reacted with 8 *M* nitric acid at 95°C for 1 day; (c) for 2 days; (d) for 3 days ($HNbO_3$).

Thermogravimetric analyses were run for $HNbO_3$ and $HTaO_3$ in an argon atmosphere. The results are shown in Fig. 2. X-ray diffraction measurements of the dehydrated products showed them to be amorphous. On prolonged heating at higher temperatures (800–1000°C), the amorphous products transformed to the equilibrium forms of the oxides M_2O_5.

Discussion

$HNbO_3$ and $HTaO_3$ can be considered to have either the perovskite or the ReO_3 structure, depending on whether they are written HMO_3 or MO_2OH. The latter formula stresses their relationship with NbO_2F and TaO_2F (*13*), with which they are isomorphous. However, the HMO_3 formula emphasizes their derivation via ion exchange from $LiMO_3$, and thus is preferred for the purposes of this paper. Certainly $HNbO_3$ and $HTaO_3$ differ from cubic perovskites such as $KTaO_3$ in that the *A* ion (H^+) cannot be centered in the MO_3 cavity; the O–H distance in that case (2.70 Å) would be unrealistically large. Since the symmetry is cubic, the proton must be disordered over a large number of sites in the unit cell. Of course, since the hydrogen is a poor scatterer of X rays, it is possible that there is some proton ordering which was not observed. However, if the proton were completely ordered, one would expect the metal–oxygen distances to be different enough to cause superstructure reflections or splitting of the diffraction lines, which was not seen. A planned neutron diffraction study of $DNbO_3$ is expected to resolve this question.

The high symmetry of the HMO_3 structure, with many more available proton sites than protons to fill them, suggested the possibility that these materials could be fast-proton conductors. However, a ^1H NMR spectrum of $HNbO_3$ at room temperature showed that this is not the case. The linewidth of the proton signal gave 10^{-6} (ohm-cm)$^{-1}$ as an upper limit to the ionic conductivity. This result is perhaps not surprising

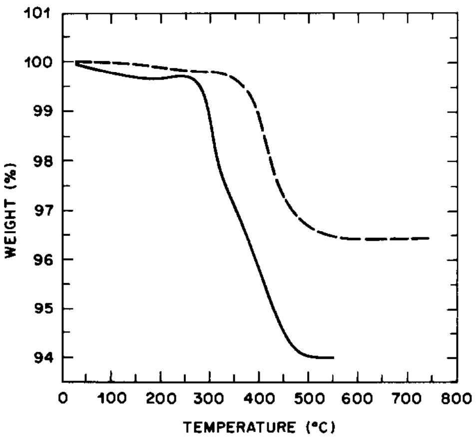

FIG. 2. TGA data for $HNbO_3$ (solid line) and $HTaO_3$ (dashed line). Heating rate was 10°/min.

since fast-proton conductors generally have considerably higher water contents than do $HNbO_3$ and $HTaO_3$.

There are few examples of crystalline niobium or tantalum hydrous oxides to compare with $HNbO_3$ and $HTaO_3$, because most of these compounds are amorphous gels. Two types of crystalline hydrous oxides have been reported: Nb_3O_7OH (*14*), made by hydrothermal growth in acid, and $H_4OM_2O_6$ (*15, 16*) (M = Nb, Ta), prepared via ion exchange from $TlMO_3$. Nb_3O_7OH is similar to $HNbO_3$ and $HTaO_3$ in that it has an ReO_3 shear-related structure, and is isomorphous with an oxyfluoride (Nb_3O_7F). $H_4ONb_2O_6$ and $H_4OTa_2O_6$ resemble $HNbO_3$ and $HTaO_3$ in that they are also made via ion exchange in acid solutions, but they are defect pyrochlores and thus are structurally different. Also, the ion exchange reaction converting $TlMO_3$ ($Tl_2M_2O_6$) to $H_4OM_2O_6$ does not involve as extensive a structural change as does the $LiNbO_3$ to perovskite transformation.

Since the change from the rhombohedral $LiNbO_3$ structure to the cubic perovskite structure is fairly drastic, one might ask whether the $LiMO_3$ to HMO_3 reaction is in fact topotactic ion exchange, or merely a dissolution of $LiMO_3$ in acid followed by precipitation of HMO_3 from solution. The fact that $LiNbO_3$ and $LiTaO_3$ crystals are etched by hot concentrated acids seems to support the latter possibility. However, the observation that the $LiNbO_3$ powder pattern shifts continuously during the initial part of the reaction (Fig. 1) indicates the existence of a rhombohedral solid solution, $Li_{1-x}H_xNbO_3$. Thus topotactic ion exchange definitely takes place, at least during this phase of the reaction. Also, attempts to grow $HNbO_3$ from solution by boiling Nb_2O_5 in concentrated acids were not successful. Therefore we think it safe to say that $HNbO_3$ and $HTaO_3$ are formed by ion exchange, not dissolution–precipitation.

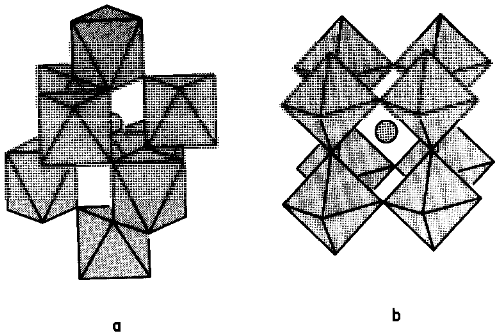

FIG. 3. Perspective drawings of equivalent portions of the (a) $LiNbO_3$ and (b) perovskite structures, showing the BO_6 octrahedral units and A ions (shaded circles). In (a) the hexagonal c axis is approximately vertical; in (b), the (100) direction is vertical.

Figure 3 illustrates the perovskite and $LiNbO_3$ structures. Both are ABO_3 structures consisting of BO_6 octrahedral units sharing corners, with A ions occupying interstices of the BO_3 network. In the cubic perovskite structure the B–O–B angles are 180°, and there is one large interstice per BO_3 unit; an A ion in this site has 12-fold coordination by oxygens. In the $LiNbO_3$ structure the oxygens approximate hexagonal closest packing; the B–O–B angles are close to 157°, and there are two octrahedral interstices per BO_3 unit. The Li^+ ion in $LiNbO_3$ occupies one of these sites, while the other remains empty. Polarity reversal in ferroelectric $LiNbO_3$ basically amounts to a shift of the Li^+ ion along the hexagonal c axis from one site to the other, along with some smaller movements of the Nb and O atoms.

Figure 4 illustrates the changes undergone during the $LiNbO_3$ to perovskite transition. As Megaw first demonstrated (*2*), the transformation can take place without breaking any Nb–O bonds or distorting the O–Nb–O angles. All that is required is a twist along the hexagonal c axis of $LiNbO_3$, or the 111 direction of the perovskite structure. In the $LiNbO_3$ to $HNbO_3$ transformation there is an overall volume expansion of 5.23%, with a 4.97% increase in the a_{hex}

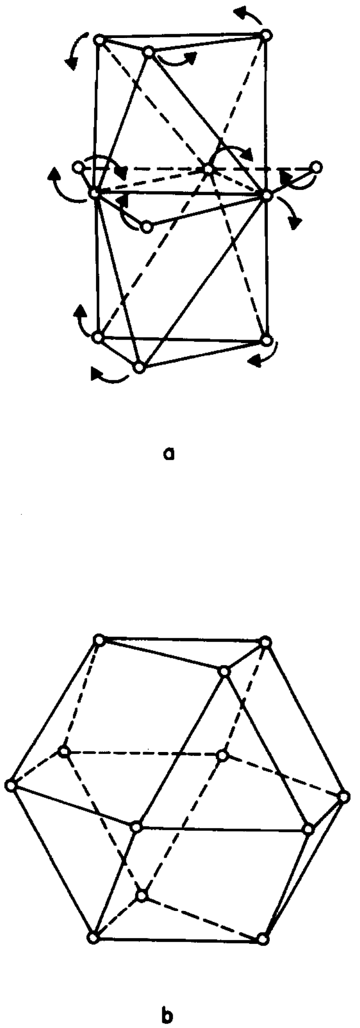

FIG. 4. Drawings showing the shapes of the cavities within the BO_3 networks of the (a) $LiNbO_3$ and (b) perovskite structures. In $LiNbO_3$ the cavity is made up of two octrahedra joined by a triangular face; one of these is occupied by a lithium ion. The perovskite structure has a single dodecahedral cavity. In (a), the orientation is approximately the same as that in Fig. 3a; in (b), the (111) direction is close to vertical. The arrows in (a) indicate the movements required to convert (a) to (b).

direction (110 cubic) and a 4.49% decrease along c_{hex}. In changing $LiTaO_3$ to $HTaO_3$, the corresponding changes are +4.80% in volume, with +4.60% along a_{hex} and −4.20% along c_{hex}.

It may at first seem surprising that replacing Li^+ (ionic radius 0.76 Å) with H^+ (effective ionic radius less than zero) (*17*) should cause an expansion in the cell volume of lightly exchanged, rhombohedral $Li_{1-x}H_xNbO_3$. However, one should remember that these radii cannot be compared directly because the two ions do not adopt the same coordination geometries. The infrared spectrum of lightly exchanged $LiNbO_3$ single crystals illustrates this difference between H^+ and Li^+ sites, and gives a clue as to why introduction of protons into this compound should cause expansion of the lattice and transition to the perovskite structure. We found the infrared spectrum of these crystals to be very similar to that reported for $LiNbO_3$ crystals containing OH^- defects caused by water uptake during the poling process (*1b*). As in that study, we found ν_{OH} to be polarized such that the O–H vector must lie within the closest-packed oxygen planes of the $LiNbO_3$ structure. Thus the most likely proton site is within the triangular face connecting octrahedral Li sites (see Fig. 4). Protons in these positions would tend to push the oxygens apart, causing a_{hex} to increase. This kind of distortion would eventually lead to a transition to the perovskite structure.

The X-ray powder patterns in Fig. 1, taken at intervals during the reaction of $LiNbO_3$ with acid, show that the structure change from rhombohedral to cubic is not continuous. Early in the reaction the $LiNbO_3$ structure does change continuously to a small extent, then undergoes an abrupt change to the cubic structure at higher H^+ concentrations. This cubic structure also shows a small amount of variability as the reaction proceeds to completion. There is evidence as well of an intermediate phase, but there are too few diffraction peaks to characterize it well. It is not surprising that the $LiNbO_3$ to $HNbO_3$ structure change is discontinuous, because intermediate structures could offer only severely distorted coordination geometries for the M^+ ions. It should be noted that the related transitions in ReO_3 (which transforms from cubic to rhombohedral on intercalation with lithium (*9*, *10*)) and $ZrFeF_6$ (which undergoes a first-order transition from rhombohedral to cubic above 208 K (*11*)) are also discontinuous.

Given the rather extensive structural changes involved in the $LiNbO_3$ to perovskite transition, it would seem doubtful that a single crystal of any size could survive this ion exchange reaction intact. In fact we have found that the particle size of $LiNbO_3$ decreases markedly during the reaction, and large crystals reacted for long periods develop badly cracked surfaces. Thus it probably will not be possible to produce $HNbO_3$ or $HTaO_3$ crystals of any appreciable size.

As heavily studied as $LiNbO_3$ and $LiTaO_3$ have been, it is surprising that such a simple reaction as ion exchange in acid was not noticed earlier, especially since crystals of these materials are often cleaned in boiling acid. From our results it seems certain that crystals treated in this way will undergo some ion exchange in a thin layer near their surface. Thus it is probable that many, if not most, of the $LiNbO_3$ and $LiTaO_3$ crystals which have been studied have had some $Li_{1-x}H_xMO_3$ present at the surface. Heat treatment of these ion-exchanged crystals would remove the hydrogen as water, leaving a lithium-deficient surface layer of $M_2O_5(Li_2O)_{1-x}$. These effects of acid cleaning may be of particular importance to surface acoustic wave and integrated optical devices, where the active region lies within a few microns of the surface.

Because $HNbO_3$ and $HTaO_3$ have cubic symmetry at room temperature, they are nonpolar and not piezoelectric. However, it is likely that the protons in these compounds will adopt a more ordered, less symmetrical arrangement at a lower temperature, or they may transform back to a $LiNbO_3$-like structure (as $ZrFeF_6$ does below 208 K (*11*)). Thus it is possible that $HNbO_3$ and $HTaO_3$ may show piezoelectric or ferroelectric behavior at low temperatures.

The ion exchange reaction used to prepare $HNbO_3$ and $HTaO_3$ may have broader application for the synthesis of new hydrous oxides from other ternary lithium oxides. Certainly $LiNbO_3$ and $LiTaO_3$, with their relatively low Li^+ mobilities, would not seem obvious candidates for this reaction; there must be other oxides which work as well or better. Ternary lithium oxides may be more likely to react than oxides of other alkali ions due to the generally higher mobility of Li^+, and also because the high hydration enthalpy of Li^+ may help drive the reaction. For example, we found that $NaNbO_3$ did not show any appreciable ion exchange in hot acids, even though its structure is closer to the $HNbO_3$ structure than is the $LiNbO_3$ structure. This ion exchange reaction could be a useful tool in the preparation of new proton conductors or ferroelectrics.

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