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# First Total $H^+/Li^+$ Ion Exchange in Garnet-Type $Li_5La_3Nb_2O_{12}$ Using Organic Acids and Studies on the Effect of Li Stuffing

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*Supporting Information*

**ABSTRACT:** Garnet-type $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ ($x$ = 0, 0.5, 1) was prepared using a ceramic method, and $H^+/Li^+$ ion exchange was performed at room temperature using organic acids, such as $CH_3COOH$ and $C_6H_5COOH$, as proton sources. Thermogravimetric analysis showed that $H^+/Li^+$ ion exchange was nearly (100%) completed using the $x$ = 0 member with $CH_3COOH$, while it proceeded to about 40% for $x$ = 0.5 and 13% for $x$ = 1. In $C_6H_5COOH$, proton exchange proceeded to about 82% for $x$ = 0, ~40% for $x$ = 0.5, and ~25% for $x$ = 1. Similar proton-exchange trends were reported in $H_2O$, where ion exchange occurs more readily for garnets with lower Li content in $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$, that is, when excess Li ions preferentially reside in the tetrahedral sites of the garnet structure.

In recent years, various Li-containing materials have become of interest because of their possible applications in all-solid-state Li-ion batteries as an alternative energy source. The ion-exchange properties of various solid Li-ion electrolytes have recently been explored, particularly, the substitution of protons for Li ions to understand the Li occupation in the structure. For example, Boulant et al. recently demonstrated the ion-exchange ability in perovskite, $La_{(2/3)-x}Li_{3x}TiO_3$, using $H_2O$ as an exchange medium.[1] A topotactic reaction was achieved that gave a novel proton-containing perovskite-type phase. They later demonstrated that the ion-exchange reaction also occurs in ambient air over an extended period.[2] Several reaction mechanisms were proposed, including the formation of LiOH, which reacts with ambient $CO_2$ and forms $Li_2CO_3$.

Because of the high Li-ion conductivity of garnet-type metal oxides, much research has been put into investigating the crystal structure and conduction mechanism.[3−7] In Li-stuffed garnet-type electrolytes, the Li ions typically reside in the tightly bound tetrahedral sites and the loosely bound octahedral sites.[8] Nyman et al. performed $H^+/Li^+$ exchange on garnet-type $Li_5La_3Ta_2O_{12}$ and found using nuclear magnetic resonance (NMR) technique that the tetrahedral sites were more involved in the exchange process.[9] Likewise, we have also found greater exchange in $Li_5La_3Nb_2O_{12}$, where Li ions reside primarily in the tetrahedral sites, than in $Li_6BaLa_2Nb_2O_{12}$, where they are mainly located in the octahedral sites.[10] In addition, we demonstrated the reversible nature of the $Li^+/H^+$ ion-exchange reaction, to the extent where the original conductivity of the parent compound can be reproduced.[10] Galven et al. have also shown $H^+/Li^+$ exchange on tetragonal garnet, $Li_7La_3Sn_2O_{12}$, using a $C_6H_5COOH$ and $C_2H_5OH$ solution.[11]

Our recent work[10] has shown that high concentrations of HCl (p$K_a$ = −7) would decompose the garnet-type structure; we had yet to investigate with weak acids. The objective of the present study was to demonstrate if the $H^+/Li^+$ ion-exchange reaction could be done in media other than $H_2O$, such as $CH_3COOH$ (p$K_a$ = 4.7) and $C_6H_5COOH$ (p$K_a$ = 4.2). The trend in percent ion-exchange completion for garnet-type $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ ($x$ = 0, 0.5, 1) in $H_2O$ is compared with that for organic acids. This study has shown that $H^+/Li^+$ ion exchange using $CH_3COOH$ and $C_6H_5COOH$ was successful.

Parent compounds, $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ were synthesized by a ceramic method using stoichiometric amounts of high-purity $LiNO_3$ (99%, Alfa Aesar), $Ba(NO_3)_2$ (99%, Alfa Aesar), $La_2O_3$ (99%, Alfa Aesar), and $Nb_2O_5$ (99.5%, Alfa Aesar), as reported in the literature.[12,13] These powders were placed into a ball mill (Pulverisette, Fritsch, Germany) with 2-propanol and zirconia balls to mix for 12 h at 200 rpm, reversing direction every 1 h. The solvent was then evaporated, and the resulting powders were collected and placed in an alumina crucible to heat at 700 °C for 6 h. After cooling, the powders were placed back into the ball mill for another 12 h. After solvent evaporation, the powders were pressed under isostatic pressure for about 5 min to form pellets (1 cm diameter and 2 cm length) and sintered at 950 °C for 24 h in air.

Sintered pellets were crushed, and about 10 g was placed in a flask. $H^+/Li^+$ ion-exchange reactions with $CH_3COOH$ were done by adding 100 mL of glacial $CH_3COOH$ (99.7%, BDH). $C_6H_5COOH$ reactions were done by dissolving 10 g of $C_6H_5COOH$ (99.5%, BDH) in 100 mL of $C_2H_5OH$, giving a 0.8 M solution, using a lower concentration for the stronger acid. After the solutions were stirred for 4 days at room temperature, powders were then collected by vacuum filtration and washed with their respective acid solutions. The powders were then dried under air at 80 °C.

Powder X-ray diffraction (PXRD; Bruker model D8, Cu K$\alpha$ radiation, 40 kV, 40 mA), was measured at room temperature with a 2$\theta$ step scan width and a counting time of 6 s to analyze the phase of the product compared to the parent compounds. Thermogravimetric analysis (TGA; Mettler Toledo Thermal Analysis, TGA/DSC1/1600HT) was performed at 25−800 °C in $N_2$ (10 °C/min) to study weight loss. Fourier transform infrared spectroscopy (FTIR; Varian model 7000) was performed using ground KBr, dried continuously in a vacuum

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oven at 150 °C, and a powder sample dispersed in KBr was measured. Scanning electron microscopy (SEM; Philips model XL30) was used to study the crystallite size and morphology.

The garnet-type compounds under investigation have a body-centered-cubic lattice and belong to space group $Ia\bar{3}d$.[9,12] The PXRD patterns for as-prepared $Li_{5.5}Ba_{0.5}La_{2.5}Nb_2O_{12}$ and $Li_6BaLa_2Nb_2O_{12}$ are not shown because they are known to have the same garnet-type structure.[10] Figure 1 displays the XRD patterns for $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ samples following treatment with $CH_3COOH$ (see Figure S1 in the Supporting Information (SI) for $C_6H_5COOH$). The patterns are similar to that of the parent compound and show that the crystal structure is maintained after acid treatment. Parent compounds exhibit lattice parameters of 12.757(3), 12.842(2), and 12.927(3) Å for $x$ = 0, 0.5, and 1, respectively. Cell constants were found to be 12.735(6), 12.786(1), and 12.800(3) Å for $x$ = 0, 0.5, and 1, respectively, after $CH_3COOH$ treatment. Similarly, cell constants of 12.722(2), 12.799(9), and 12.838(9) Å were obtained for $x$ = 0, 0.5, and 1, respectively, for $C_6H_5COOH$-treated samples. We believe that H may be incorporated into the initially occupied Li sites, but the exact structure could not be meaningfully determined in this study. The products of the ion-exchange reaction were heat-treated at 700 °C for 2 h to demonstrate heat decomposition of the structure at elevated temperatures. As expected, the resulting PXRD patterns shown in part v of Figures 1 and S1 in the SI show the formation of perovskite-related "$La_2LiNbO_6$" [Joint Committee on Powder Diffraction Standards (JCPDS) File Card No. 040-0895]. There may be trace amounts of Li present, but the exact composition of the product cannot be determined with certainty. Other decomposition phases in the $La_2O_3-Nb_2O_5$ system may also be present. As previously reported,[10] the structure will decompose if the extent of ion exchange is far enough that the majority of Li ions have been replaced by protons, which are less stable to heat. Li-containing garnets are known to retain their crystal structure at temperatures up to 900−1000 °C.[3410]

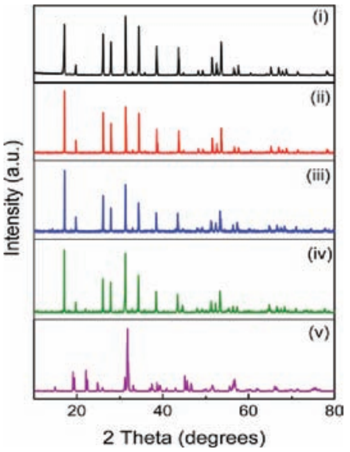

**Figure 1.** PXRD patterns of as-prepared (i) $Li_5La_3Nb_2O_{12}$, $CH_3COOH$ treated, (ii) $Li_5La_3Nb_2O_{12}$, (iii) $Li_{5.5}Ba_{0.5}La_{2.5}Nb_2O_{12}$, and (iv) $Li_6BaLa_2Nb_2O_{12}$ and (v) the sample in pattern ii treated at 700 °C for 2 h in air.

Following confirmation of $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ phase formation after treatment with organic acids, further characterization of the exchanged compounds was done using TGA. Successfully performing the ion-exchange reaction would give the respective H analogues, which are expected to decompose at elevated temperature (Figures 1 and S1 in the SI). The TGA results show weight loss at about 300−500 °C (Figures 2 and S2 in the SI). The observed very slight break in the plot [Figure 2(i), left] may be due to loss of H from the tetrahedral sites versus the octahedral sites. This weight loss observed can be used to determine the H content of each sample. The $x$ = 0 species shows about a 5.6% weight loss with $CH_3COOH$, corresponding to ~100% completion of the ion exchange, giving a nominal chemical composition of "$H_5La_3Nb_2O_{12}$". This was greater than what was observed for $C_6H_5COOH$ and even higher than previously reported using $H_2O$.[10] Weight loss was not observed below 100 °C, suggesting that the sample was properly dried well before measurement and surface $H_2O$ or unwashed organic acids were not present. Weight loss was completed at about 600 °C and stayed nearly constant thereafter (Figures 2 and S2 in the SI).

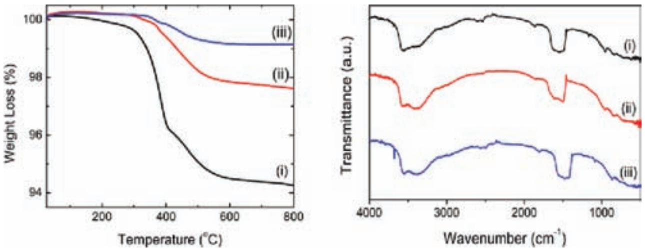

**Figure 2.** TGA (left) and FTIR (right) of as-prepared (i) $Li_5La_3Nb_2O_{12}$, (ii) $Li_5La_3Nb_2O_{12}$, and (iii) $Li_{5.5}Ba_{0.5}La_{2.5}Nb_2O_{12}$, all treated with $CH_3COOH$.

The $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ compounds show a trend in TGA similar to what was previously observed when using $H_2O$ as a proton source, where $x$ = 0 showed the greatest exchange, followed by $x$ = 0.5, and then $x$ = 1. When using $CH_3COOH$ or $C_6H_5COOH$ on the $x$ = 0.5 species, the ion-exchange reaction proceeded to ~40% completion, giving "$Li_{3.3}H_{2.2}Ba_{0.5}La_{2.5}Nb_2O_{12}$" under both treatments. For $x$ = 1, using $CH_3COOH$ gave only "$Li_{4.5}H_{1.5}BaLa_2Nb_2O_{12}$", indicating ~13% ion exchange, while $C_6H_5COOH$ was slightly better with "$Li_{4.2}H_{1.8}BaLa_2Nb_2O_{12}$", specifying ~25% completion (Figures 2 and S2 in the SI).

O'Callaghan and Cussen have recently shown in a neutron diffraction study on closely related $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$ ($x \leq 1.6$) that excess Li ions in the garnet structure preferentially occupy the tetrahedral sites (24d; ca. 80%) for members with lower Li content.[14] Excess Li also occupies one additional distorted octahedral site (48g; ca. 40%), which is preferentially occupied in members with greater Li content. The tetrahedral sites bind Li more tightly and are considered the Li-ion trapping sites, while the octahedral site binds Li more loosely and Li ions here are believed to be responsible for fast Li-ion conduction in these garnets.[9] In the $x$ = 1.6 garnet, they report that the tetrahedral sites are mainly vacant (~14%), while the octahedral site is more preferentially filled (~57%).[14] Our previous report showed that $H^+/Li^+$ ion exchange proceeds to a greater extent for $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ garnets with lower Li content; that is, it is easier to extract Li in this reaction when more reside in tetrahedral sites. During the extraction process, it seems that the protons prefer to reside in the smaller tetrahedral sites. Nyman et al. have reported similar observations from NMR studies, where ion-exchanged Li ions were those from the framework sites.[4]

For additional chemical characterization, FTIR was performed to further confirm the presence of H incorporated into the crystal structure. In Figures 2 and S2 in the SI for the garnet compounds after acid treatment, all spectra show a distinct broad hydroxide (OH) band in the 3300−3600 cm$^{-1}$ region. The products were dried very thoroughly as seen in the TGA data, where no weight loss was observed below 300 °C, indicating that the OH stretches in the FTIR are due to vibrations within the crystal structure. Also, the FTIR spectra for as-prepared Li garnets showed several bands corresponding to the metal−oxygen bonds, and there were no OH bands.[10]

The two organic acids investigated have slightly different effects on the Li garnet compounds under study (Table 1). On the basis of TGA data (Figures 2 and S2 in the SI), while they seem to have equal effects on ion exchange for the $x$ = 0.5 member, $CH_3COOH$ appears to be more effective for $Li_5La_3Nb_2O_{12}$ and $C_6H_5COOH$ seems to be more effective for $Li_6La_2BaNb_2O_{12}$. Typical SEM images of acid-treated $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ are shown in Figures 3 and S3 in the SI.

**Table 1. Percent Completion of $H^+/Li^+$ Ion-Exchange Reactions for $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ Using Organic Acids and $H_2O$[10] as Proton Sources**

| $x$ | $H_2O$ | $CH_3COOH$ | $C_6H_5COOH$ |
|---|---|---|---|
| 0 | 89 | 100 | 82 |
| 0.5 | 46 | 40 | 40 |
| 1 | 20 | 13 | 25 |

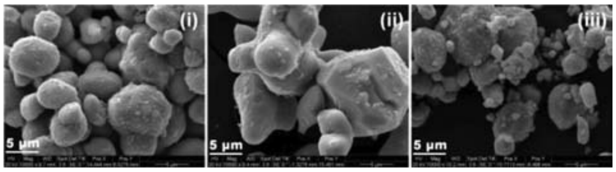

**Figure 3.** SEM images of $CH_3COOH$-treated (i) $Li_5La_3Nb_2O_{12}$, (ii) $Li_{5.5}Ba_{0.5}La_{2.5}Nb_2O_{12}$, and (iii) $Li_6BaLa_2Nb_2O_{12}$.

Several batches of each compound were synthesized, and TGA was performed multiple times, with trends being quite consistent. We speculate that the formation of lithium acetate seems to facilitate Li extraction from the garnets in $CH_3COOH$, more so than lithium benzoate formation in $C_6H_5COOH$. On the basis of TGA data and the Li-stuffed garnet structure proposed by Goodenough and Kim[6] and Cussen,[5,8] it seems that $C_6H_5COOH$ allows Li extraction from the octahedral sites with more ease. However, the exact role of organic acids and the effect of the particle size on ion exchange and the remaining Li ions and proton sites in the exchanged products need to be addressed. Determination of the actual structure for the proton-exchanged garnet is nontrivial;[15] however, work on deuterium-exchanged garnets is under progress in a collaborative work. Proton conductivity is also under investigation by performing ion-exchange reactions directly on the pellet form. The present work demonstrates that the most effective method of producing the H analogue of a Li garnet would be to use the $x$ = 0 member and undergo treatment with $CH_3COOH$, giving almost a pure H-containing garnet.

In summary, $H^+/Li^+$ ion-exchange reactions with garnet-type $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ using weak organic acids such as $CH_3COOH$ and $C_6H_5COOH$ were successful. The TGA results showed that the reaction proceeded to approximately 100%, 40%, and 13% completion for the $x$ = 0, 0.5, and 1 species, respectively, using $CH_3COOH$. The reaction went to about 82%, 40%, and 25% for the $x$ = 0, 0.5, and 1 species, respectively, using $C_6H_5COOH$. The same trend among the three members, compared to using $H_2O$ as an exchange medium, was observed but resulted in slightly different exchange values. PXRD data showed that the cubic crystal structure was preserved throughout the reactions. FTIR results also show the presence of OH in the products. Overall, ion exchange of $Li_{5+x}Ba_xLa_{3-x}Nb_2O_{12}$ was successful using organic acids.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

PXRD data and patterns, TGA, FTIR, and SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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