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Reinvestigation of the Total Li^+/H^+ Ion Exchange on the Garnet-Type $Li_5La_3Nb_2O_{12}$

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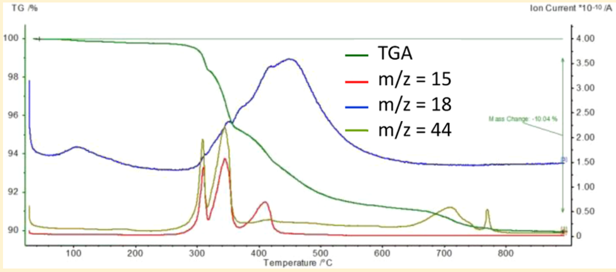
ABSTRACT: Li^+/H^+ exchange was performed on $Li_5La_3Nb_2O_{12}$ using CH_3COOH. After X-ray powder diffraction experiments to check the quality of $Li_{5-x}H_xLa_3Nb_2O_{12}$, the chemical formulation was determined by thermogravimetric analysis coupled with mass spectrometry and flame photometry. The results showed unambiguously that the Li^+/H^+ exchange was not total and that some CH_3COOH remained in the sample. Raman experiments revealed in addition that the organic contribution on the spectrum was due either to metal acetate or to ionic bond to the crystal.



INTRODUCTION

The garnet compounds correspond originally to natural silicates of general formula $A_3B_2Si_3O_{12}$, where the A^{2+}, B^{3+}, and Si^{4+} ions are respectively located in 8-coordinated, octahedral, and tetrahedral sites. The cubic cell is body centered with a cell parameter close to 13 Å and contains eight formula units. Since their discovery, the garnets have been extensively studied because of their magnetic properties and of the structure flexibility, which allows various chemical substitutions leading to a large number of phases. Among them, lithium garnet phases have an important place in the literature because they exhibit interesting ionic conduction by Li^+ ions, making them potential electrolytes in future all solid-state lithium batteries. Compared to the conventional garnet stoichiometry, some of these phases contain additional lithium cations, leading to the formulations $Li_xA_3B_2O_{12}$ with $3 \leq x \leq 7$. These lithium garnet phases crystallize most often in the cubic space group $Ia\overline{3}d$, but a few of them crystallize in the tetragonal system as $Li_7La_3Sn_2O_{12}$ or $Li_7La_3Hf_2O_{12}$, for example.[1,2]

While the garnet phases were usually considered as chemically stable when exposed to moisture,[3,4] some authors have studied the stability of the lithium garnets[5−8] and showed that, in humid atmosphere, a spontaneous Li^+/H^+ exchange occurs while the lithium released is combined with atmospheric CO_2 to form Li_2CO_3. This reaction, leading to a new partially protonated phase $Li_{x-y}H_yA_3B_2O_{12}$, is topotactic and reversible: indeed, the new form adopts a garnet-type structure and a heating allows recovery of the mother form. This Li^+/H^+ exchange can give rise to a phase transition from tetragonal to cubic[7,8] or to a change of space group in the cubic system, as in the case of the garnet $Li_6CaLa_2Nb_2O_{12}$[6] or $Li_5La_3Nb_2O_{12}$.[8] However, the Li^+/H^+ exchange is always associated with an increase of the cell parameter whatever the considered compounds: garnets,[6−9] but also Ruddlesden−Popper layered perovskites,[10,11] or even 3D perovskites.[12] This is in any case explained by the replacement of strong Li−O bonds by weak hydrogen O−H···O bonds.

Concerning this work, the compound $Li_5La_3Nb_2O_{12}$ was published for the first time in 1988 by Mazza.[13] That same year, Hyooma and Hayashi[14] determined its structure by X-ray monocrystal diffraction data in the cubic noncentrosymmetric space group $I2_13$ and showed that lithium ions occupied two crystallographic sites. In 2003, Thangadurai et al.[15] investigated this phase with regard to the electrical properties and revealed its ionic conductor character with a bulk conductivity close to 10^{-6} S/cm at 25 °C. In 2006, Cussen[3] proposed a new structural description of $Li_5La_3Nb_2O_{12}$ in the centrosymmetric cubic $Ia\overline{3}d$ space group from powder neutron diffraction data. Three different lithium sites are revealed (one tetrahedral and two distorted octahedral), and all of them are partially occupied. In 2011, we published a complete study about the instability toward moisture of the lithium garnet $Li_7La_3Sn_2O_{12}$.[8] In this article, we also announced a forthcoming paper concerning the Li^+/H^+ exchange on $Li_5La_3Nb_2O_{12}$. The structure of this new partially protonated phase $Li_{5-x}H_xLa_3Nb_2O_{12}$ was then published one year later from powder neutron diffraction data,[7] with this phase being prepared from ionic exchange in ethanol and benzoic acid. The formulation was determined by two complementary methods: flame photometry and TGA measurement. The first technique allows the determination of the exchanged lithium quantity in the filtrate while the second one allows the determination of the quantity of proton in the new garnet form. Indeed, under heating, the loss of proton as H_2O leads to a decrease of the mass. This mass variation is then used to calculate the proton quantity present in the protonated garnet phase. In this paper, we have also observed that the Li^+/H^+ exchange feasibility is directly connected to the lithium

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stoichiometry: if the concentration of Li^+ ions is greater than what can be accommodated on the tetrahedral site commonly occupied, meaning more than three lithium ions per formula, the garnet is sensitive to humidity. In addition, whatever the garnets tested, we have never obtained a total exchange. This observation is nevertheless in contradiction with a result published the same year by Truong and Thangadurai,[16] who announced the first total Li^+/H^+ ion exchange in $Li_5La_3Nb_2O_{12}$ using glacial CH_3COOH. In their paper, the Li^+/H^+ exchange feasibility is confirmed from FTIR results with the presence of OH in the product while the exchange rate is determined from the weight loss observed by TGA measurement. No determination of the exchanged lithium quantity in the filtrate is performed. Moreover, if the X-ray powder diffraction pattern confirms that the garnet-type is preserved during the ionic exchange, the refinement of the cell parameter reveals surprisingly a very slight decrease: 12.757(3) Å for $Li_5La_3Nb_2O_{12}$ and 12.735(6) Å for the protonated form after treatment in CH_3COOH.

In this context, as it seems to us unlikely to obtain a total exchange in such experimental conditions, and taking into account the surprising cell parameter evolution observed between the mother and the protonated phases, we decided in the present work to reinvestigate the Li^+/H^+ exchange in $Li_5La_3Nb_2O_{12}$ using the same experimental conditions used by Truong and Thangadurai.[16] In this new study, the characterization of the protonated form has been done by complementary methods: an X-ray powder diffraction experiment to refine the cell parameter, flame photometry, and thermal analysis to determine precisely the chemical formulation of the exchanged garnet and Raman experiments.

■ EXPERIMENTAL SECTION

Synthesis. The mother phase $Li_5La_3Nb_2O_{12}$ was prepared using a conventional ceramic method according to the literature. Starting products (dried Li_2CO_3, dehydrated La_2O_3 and Nb_2O_5) were ground together in a stoichiometric ratio in ethanol for 30 min. An excess of 20% of Li_2CO_3 was added to compensate for the loss commonly observed at high temperature. After evaporation of the solvent, the resulting mixture was dried in an oven before pelletization and heated in an alumina crucible at 700 °C for 12 h, 800 °C for 12 h, and 900 °C for 12 h with two intermediate grindings. A last heating at 925 °C for 2 h was applied to improve the crystallinity. After each step, the purity and the crystallinity of the sample were checked by X-ray diffraction analysis.

The exchanged form $Li_{5-x}H_xLa_3Nb_2O_{12}$ was prepared by following the procedure used by Truong and Thangadurai.[16] The $Li_5La_3Nb_2O_{12}$ powder was introduced in a flask containing glacial acetic acid. The solution was maintained under stirring for 4 days at room temperature. The powder was recovered by vacuum filtration and washed with acetic acid. The filtrate of this washing step was preserved in order to determine the lithium content by flame photometry. After drying in an oven at 60 °C, the powder was analyzed.

Characterizations. In order to check the purity of the mother and protonated phases and to determine their cell parameters, we collected powder X-ray diffraction (PXRD) patterns on a PANalytical X'pert Pro diffractometer equipped with the X'Celerator detector (using Cu Kα radiation). The experimental conditions chosen for the data collection were as follows: 5−130° angular range, 0.017° step scan increment, and 225 s counting time by step. The refinements were performed with the Rietveld method[17] using the program Fullprof,[18] and the peaks shape was modeled by a pseudo-Voigt function. The points of the background level were determined manually before being refined. According to our objectives, we performed only full pattern matching refinements in order to obtain the cell parameter values of the mother and the protonated form.

To determine the lithium quantity extracted from $Li_5La_3Nb_2O_{12}$ during Li^+/H^+ exchange, a lithium content analysis of the filtrate obtained from the washing step was used. This was done using the flame emission spectrometer Sherwood 410. Standard solutions were prepared with the same acid concentration as that of the analyzed solution in order to have the most accurate result possible.

Thermal analysis between 25 and 900 °C was performed on a TGA Jupiter STA 449 F3 Netzsch instrument under Ar flow with a heating rate of 5 °C min^{-1}. To characterize the gas emitted by the sample during heating, this TGA equipment was coupled with a mass spectrometer Aëolos QMS 403C Netzsch.

The Raman spectra have been collected with a Xplora spectrometer (Horiba-Jobin-Yvon), under a microscope (x50 LF objective) using 638 nm radiation as excitation, and calibrated with the 520.2 cm^{-1} line of silicon.

■ RESULTS AND DISCUSSION

All the diffraction lines of the PXRD pattern of the mother compound $Li_5La_3Nb_2O_{12}$ can be indexed in a cubic cell using the $Ia\overline{3}d$ space group. The refinement leads to the cell parameter a = 12.7988(2) Å, in agreement with the result of Cussen[3] (12.7943(1) Å), and confirms the good crystallization and the purity of the mother phase.

The PXRD pattern of the exchanged form $Li_{5-x}H_xLa_3Nb_2O_{12}$ (Figure 1) presents thin *hkl* lines closely related to those of the garnet structure, confirming thus that the Li^+/H^+ exchange results from a topotactic mechanism. Nevertheless, we observed three weak additional lines ($2\theta° \approx 54.2$, 65.7, and 86.1) which cannot be indexed in the $Ia\overline{3}d$ space group (Figure 1). Taking into account our previous study,[7] these lines are perfectly indexed in the noncentrosymmetric space group $I2_13$, which allows explanation of all the diffraction peaks visible on the PXRD pattern. The refinement performed in this space group leads to a cell parameter of 12.8434(4) Å, implying that the cell volume increases during the Li^+/H^+ exchange: 2096.6 $Å^3$ for $Li_5La_3Nb_2O_{12}$ compared to 2118.6 $Å^3$ for $Li_{5-x}H_xLa_3Nb_2O_{12}$. This result is in agreement with various studies[6−14] performed not only on garnets but also on perovskites.

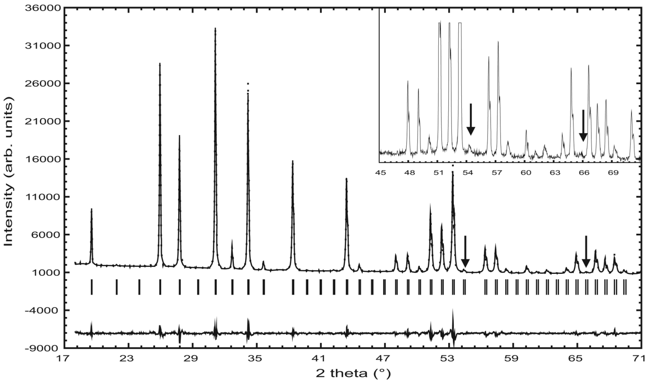

Figure 1. Observed, calculated, and difference PXRD patterns of $Li_{1.4}H_{3.6}La_3Nb_2O_{12}$ in the $I2_13$ space group. Vertical bars are related to the calculated Bragg reflection positions. (R_p = 11.2; R_{wp} = 11.3; R_{exp} = 5.70; χ^2 = 3.92).

The analysis of the lithium content in the filtrate reveals a partial exchange leading to the formulation $Li_{1.4}H_{3.6}La_3Nb_2O_{12}$ (exchange rate of 72.3%).

From the formulation obtained by chemical analysis, the expected mass variation during the thermal analysis should correspond to 4.02%. This weight loss results from a proton departure under water according to this reaction:

$$Li_{1.4}H_{3.6}La_3Nb_2O_{12} \rightarrow 1.8H_2O + \text{“}Li_{1.4}La_3Nb_2O_{10.2}\text{”}$$

The thermal analysis of the protonated garnet form (Figure 2a) shows a continuous weight loss corresponding to a total variation of 10.04%. This value is higher than the expected one and, in addition, higher than the value corresponding to a total exchange (5.63%). To attempt to understand such a result, we decided to perform a second TG experiment while analyzing the gas emitted by the sample under heating using mass spectrometry (MS). For this purpose, we followed different fragments characteristic of water (m/z = 18) and acetic acid (m/z = 15, 18, 44). Some of these results are gathered in Figure 2a. The curves reveal that the weight loss occurs between 300 and 800 °C and that it can be unambiguously attributed to both acetic acid and water departure. This means that acetic acid remains in the sample. Moreover, as its departure occurs at higher temperature (T > 300 °C) than the boiling point of CH_3COOH ($T \approx 118$ °C), this suggests that the acetic acid is most probably chemically bonded to the grains garnet. In order to obtain the weight variation corresponding only to the proton loss as H_2O, we decided to wash the exchanged sample before TG and MS experiments. For this, the sample $Li_{5-x}H_xLa_3Nb_2O_{12}$ is washed 30 min in ethanol, since CH_3COOH is soluble in ethanol. After filtration and drying 30 min in an oven, the TGA experiment coupled with the simultaneous analysis of the gas emitted is undertaken. We observe (Figure 2b) that the mass variation measured on this sample is first much lower than the first value observed (4.38% compared to 10.04%) and second in better agreement with the expected value: 4.38% for 4.02% if we take into account the formulation determined from the chemical analysis. In addition, signals only characteristic of CH_3COOH are barely visible (m/z = 15, 44). This confirms that the weight loss obtained without the washing step in ethanol (10.04%) can be partially attributed to acetic acid, meaning then that it is not possible to calculate the formulation of the exchanged garnet only from TGA measurements. As expected, the m/z = 18 is still visible in Figure 2b, and results of the proton departure under H_2O form according to the previous reaction. In addition to this signal, we observe around 770 °C a narrow peak belonging to the m/z = 44 fragment which can also be attributed to CO_2. This CO_2 departure is probably due to a spontaneous Li^+/H^+ exchange which could have occurred under ambient conditions. Indeed, it is now well-known that lithium garnets are sensitive to moisture.

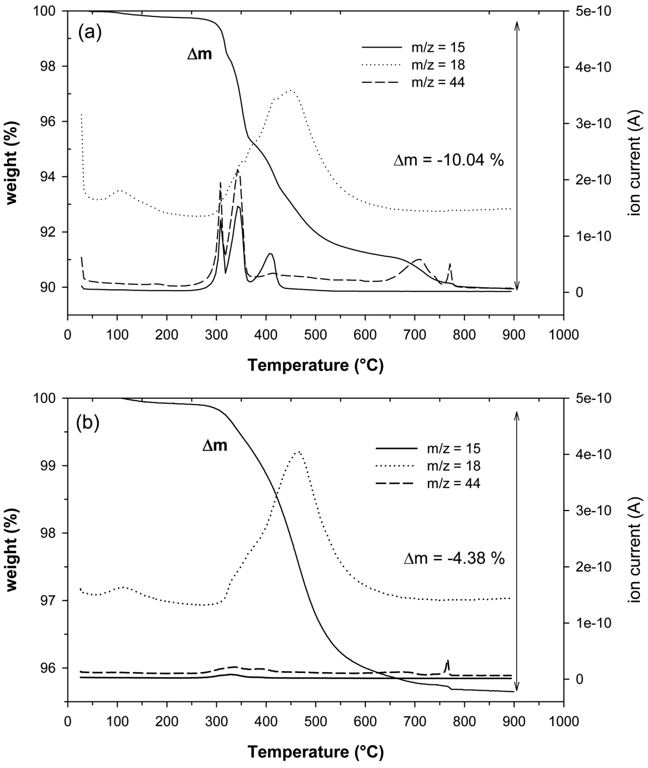

Figure 2. TGA and MS of $Li_{1.4}H_{3.6}La_3Nb_2O_{12}$ before washing (a) and after washing (b).

In order to complete this study, Raman experiments were undertaken. The Raman spectra collected just after exchange, and prior to and after rinsing with ethanol are shown in Figure 3. The former contains mainly two narrow lines at 2925 cm^{-1} and at 942 cm^{-1} that disappear after rinsing. Such signals are known as the most intense signatures of the acetic component,[19,20] with the former arising from the C−H stretching of the CH_3. The second one arises from the C−C stretching, and according to refs 21−23, it is expected at about 892 cm^{-1} in pure CH_3COOH or in the presence of water, and above ≈920 cm^{-1} in CH_3COO^- in aqueous solution[21,22] or in crystals.[22,24,25] So, the organic contribution before rinsing arises whether from metal acetate or from ionic bond to the crystal.

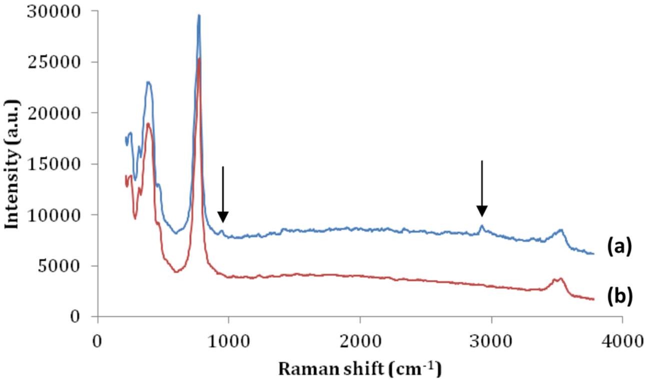

Figure 3. Raman spectrum of the sample just after lithium exchange ((a), shifted for the sake of clarity), and after subsequent rinsing with ethanol (b). The arrows on the spectrum point out the most intense lines characteristic of CH_3COO^- at 2925 cm^{-1} and 942 cm^{-1} for the C−H and C−C vibrational stretching vibrations, respectively.[19−23]

■ CONCLUSION

In summary, when the Li^+/H^+ exchange is performed in CH_3COOH, some acid remains in the sample. A washing step in an appropriate solvent must then be applied after the exchange in order to remove the acid and obtain the true exchange rate from TGA measurement. The Raman experiments have shown, in addition, that the organic matter was present either under metal acetate or under CH_3COO^- bound to the surface.

In addition, we observed that a short treatment (2 h) at 200 °C performed on the exchanged garnet improves the crystallinity of the sample.

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Notes

The authors declare no competing financial interest.

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