Synthesis and Topochemical Manipulation of New Layered Perovskites

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Synthesis and Topochemical Manipulation of New Layered Perovskites

A Dissertation

Submitted to the Graduate Faculty of the
University of New Orleans
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy
in
Chemistry
Solid State

By

Léa Gustin
B.S., Heriot-Watt University, 2010
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May, 2016
To my family and those who were always there for me,

no matter where they were in the world.
Acknowledgements

I would like to start by thanking my advisor Professor John B. Wiley. I would not be here if it wasn’t for him taking me in his group as an undergrad coming for internship 7 years ago and making me realize that I could do much more than I thought. I guess I just could not stay “far far away” and was meant to come back to this group. Thank you so much for guiding me, listening to my many (random) stories and complaints while putting me on the right path, whether in the lab by teaching me new things and giving advice or just in life in general. I cannot thank you enough for your trust, your patience, all the freedom you gave me and for all the opportunities you offered me. I learned so much with you, I can’t believe it has been that long. Thanks Boss!

Elisha, you have been one of the most influential persons I have ever met. Thank you for always being there for me, listening to me, guiding me, calling me out when I was being lazy (I definitely needed it), for the crazy memories and some of the best days I have had. You taught me how to believe in myself, when it came to my science and for everything else. From mentor to colleague, friend and family I would not have made it that far without you.

Thank you to all my group members, past and present: Sanjaya, CJ, Girija, Elisha, Yuan, Jianxia, Jin-Hee, Debasish, Shiv, Dariush, Taha, Sarah, Treva, Sara, Clare, Lexis, Shahid, Mark and all the undergrads that joined our group at some point. Thanks for the moral support, the help you gave me. We are like a big family, with good and bad days and I finish this Ph.D. with so many memories. P4P!!!

I was fortunate enough to join Prof. Kageyama’s group for two months. I would like to thank him for welcoming me, all the instructive conversations that led to some of the results presented in this dissertation. Thanks to his group members, in particular Dr. Cedric Tassel for helping me with refinement, Satoko and Tomoko for their help and making my stay so great. I would also like to thank Prof. Shimakawa and Yoshiteru Hosaka from Kyoto University for their help with the Mössbauer spectroscopy. This iron project would have not gone as far without you.
I would like to recognize the students I mentored throughout the years as they contributed to the work in this dissertation: Carole Lepoix, Amy Pressley, Jérome Lefebvre, Maxime Brault, Clare Davis-Wheeler and Van Vu.

Thank you to Dr. Spinu and his group members Dr. Jose Vargas, Shankar Khanal, Ali Radmanesh, and Daniel Adams for their help with all the magnetic measurements.

Thank you to everybody in the Chemistry Department, for the financial support, the technical one and definitely the moral one.

Support from the National Science Foundation (under grant DMR-1005856) is gratefully acknowledged.

To Dr. Hauck, Dr. Gallagher and Sean Hickey, being a TA for so many semesters could have been the worst part of my Ph.D., but I am so grateful for the trust and the freedom you gave me to have the best experience teaching those labs.

I could not have survived grad school without my friends, from the department and outside. I am thankful for all the persons I met along the way but to only name a few: Richie and Maria (forever the 3 musketeers), Sarah (IUT en force!), Ujwal, Adam, Edwin, the Nepali gang: Puja, Sonu, Zenisha, Binay, both Krishna’s, Emily, Lety, Aurélie and my friends back home who were always “here”: Vince, Maxou, Mymy, Laulau, Daddy, Marine, Pascalie, Alex, Manu, Binome, Brunette, Berton; Thank you guys!

Last but not least (le meilleur pour la fin) I would like to thank my family. Thank you so much for supporting me thousands miles away, letting me explore the world without ever complaining about me leaving and for always having the right word to keep me going when it became hard. Mamounette, Papou, P’tit Frère, Papy, I hope I made you all proud.
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Abstract

Metastable layered perovskites containing interlayer transition metals can readily be obtained by simple ion exchange reactions on receptive hosts, such as those of the Dion-Jacobson and Ruddlesden-Popper structure types. In this work, we focused on adding to the library of layered perovskites by not only creating new compounds, but by also showing their ability to be further manipulated, and by studying the stability of the series through thermal behavior studies.

The reactions with transition metal halides are particularly interesting since they often lead to novel architectures and magnetic behavior. On subsequent heat treatment, these exchange products typically decompose to thermodynamically more stable phases. The newly synthesized spin glass-like material, FeLa$_2$Ti$_3$O$_{10}$, obtained by ion exchange of Li$_2$La$_2$Ti$_3$O$_{10}$ with FeCl$_2$ at 350 °C, behaves differently. When heated to 700 °C, the compound undergoes a significant cell contraction ($\Delta c \approx -2.7$ Å) with an increase in the oxidation state of iron present in the interlayer that has not been observed before in such compounds. Efforts were also made to synthesize new series of compounds, here MSrTa$_2$O$_7$ (M= Co and Zn), with vacancies in the interlayer that could lead to future topochemical manipulations.

The ability to vary the composition of different phases to form solid-solutions through atomic substitution at the A or B sites with ions of similar or different charge can lead to new structures as well an enhancement of the properties of the original compound or new ones. The synthesis and characterization of the new mixed A-cation containing layered perovskite RbLaNaNb$_3$O$_{10}$, where La$^{3+}$ and Na$^+$ share the same site in the perovskite slab and RbLaCaNb$_2$MnO$_{10}$ that exhibits an ordering of the B site with Mn in the center of the perovskite slab will be presented. Further topochemical manipulation of these phases via ion exchange
reactions at low temperatures (< 500 °C), lead to the new series A’LaNaNb$_3$O$_{10}$ and 
A’LaCaNb$_2$MnO$_{10}$ where A’= H, Li, Na, K and CuCl.

Keywords: layered perovskites, synthesis, topochemistry, ion exchange, X-ray powder

diffraction
Chapter 1

Introduction and Background

1.1 Perovskites and Layered Perovskites

Since their discovery in 1839 by Gustav Rose, perovskite compounds have received much interest due to their diverse properties, applications, and wide chemical variations related to their very tunable structure. The properties exhibited by perovskites and perovskite related compounds are numerous; from high temperature superconductivity, colossal magnetoresistance, catalytic activity, and interesting ferroelectricity.

The ideal perovskite oxide structure described as ABO$_3$ (e.g. CaTiO$_3$) where A is an alkali metal, an alkaline earth metal or a rare-earth metal, and B is a transition metal, is the basis of many families of compounds. The basic perovskite structure consists of a close-packed array of A cations and O anions, with B cations filling one fourth of the octahedral sites. It can also described as 8 corner-sharing BO$_6$ octahedra surrounding the central A cation as shown in Figure 1.1.

![Image of Ideal perovskite structure](image)

Figure 1.1 Ideal perovskite structure
There are several variations of the perovskite structure including a series of layered-perovskites. The Dion Jacobson (DJ) and Ruddlesden-Popper (RP) family members, are two common layered perovskites that have the general formulas \( A\[A'_{n-1}B_nO_{3n+1}] \) and \( A_2[A'_nB_nO_{3n+1}] \), respectively, where \( n \) is the number of perovskite slabs. The main difference between the two structures presented in Figure 1.2 resides in the interlayer. The DJ series have one A cation interconnecting the perovskite slabs where the RP phases have two.

![Figure 1.2](image-url) Representative layered perovskite structures. (a) Dion-Jacobson RbLaNb_2O_7 and (b) Ruddlesden-Popper K_2SrTa_2O_7

Most layered perovskites have significant ionic character due to the interaction between the different slabs and interlayer units, as well as strong covalent character within the slab itself. In every case, the nature of the B cation strongly influences the different properties of the compounds, greatly contributing to the electronic and magnetic properties of each. For example,
manganese oxides with perovskite related structures have been reported to exhibit giant magnetoresistance properties due to the mixed valency of the manganese in the perovskite layer.\textsuperscript{3}

These two perovskite-related structures have attracted considerable attention in the past decades not only due to their properties, but also their reactivity to topochemical manipulations that led to numerous new layered-materials not obtainable through conventional methods.

1.2 Solid State Synthetic Methods

Layered perovskites can be synthesized using different reaction pathways. The most common one is the ceramic method ("heat and beat") that can require high temperatures, long reaction times, and in most cases very fine mixing to insure good diffusion of the ions among the reagents. Intermediate grindings are often required to bring fresh reactant surfaces into contact, so the whole process is labor intensive. Ceramic methods, while advantageous in many preparations, are limited as to the synthesis of metastable compounds. High temperatures could lead to decomposition and less control of a small window available to obtain kinetically stable compounds. Moreover, ceramic methods present important limitations concerning structure especially when the target is to maintain the overall structure of the starting material; high temperatures favor a more thermodynamically stable product which allows little room for structure manipulation to target new designed materials.

In order to create new compounds, soft chemistry (chimie douce) can be used through topochemical methods.\textsuperscript{9} Such techniques can lead to the formation of new layered compounds maintaining the overall, important, structural features of the starting material. In order to preserve the overall structures, the reactions are carried out at relatively low temperatures (\(<500^\circ\text{C}\)). Reactions can take place in open air or under different atmospheres (\(\text{O}_2\), \(\text{Ar}\), \(\text{H}_2\) or also
under vacuum depending on the target reaction). Figure 1.3 gives an overview of a variety of topochemical manipulations that can be carried out on layered perovskites.⁹

![Figure 1.3 Different examples of topochemical manipulations](image)

**Figure 1.3** Different examples of topochemical manipulations
Ion exchange (IE) reactions are a common topochemical synthetic method. It entitles the replacement of weakly bound cations (or anions) for other ionic species as in the proton exchange of $\text{K}_2\text{SrTa}_2\text{O}_7$ to obtain $\text{H}_2\text{SrTa}_2\text{O}_7$, which in turn enhanced the photocatalytic properties of the material.\textsuperscript{10} Monovalent ion exchange reactions have been extensively studied for both DJ and RP phases\textsuperscript{11–16} but the reactions are not limited to an exchange of cations with the same charge. Viciu et al. reported reactions with divalent cations.\textsuperscript{17} The 2-for-1 exchange using $\text{MBr}_2$ (M=Fe, Ni) as metal source led to the formation of $\text{M}_{0.5}\text{LaNb}_2\text{O}_7$ at 350 °C. Another example of this type of topochemical manipulation includes the co-exchange of cations and anions to form copper halide networks between the perovskites slabs as in $(\text{CuCl})\text{Ca}_2\text{Nb}_3\text{O}_{10}$.\textsuperscript{18} A very appealing aspect of the ion exchange reactions is the fact that they allow one to create a bridge between the different families of layered perovskites. In 1999, Hyeon and Byeon reported an example of ion exchange of two alkali metal cations by small transition-metals when obtaining the new DJ phase $\text{M}^{\text{II}}\text{La}_2\text{Ti}_3\text{O}_{10}$ (M= Co, Cu, and Zn) from the RP layered oxide $\text{Na}_2\text{La}_2\text{Ti}_3\text{O}_{10}$.\textsuperscript{19} In doing so, they opened the door to further chemistry as the aliovalent ion exchange created vacancies in the interlayer that could be used for further topochemical manipulations.

Intercalations (oxidative, reductive, and neutral) and deintercalations are methods that are also widely applied due to their ability to produce mixed valent products, a feature which can lead to interesting new magnetic and electronic materials. The Dion-Jacobson phase, $\text{RbLaNb}_2\text{O}_7$, can undergo reductive intercalation and form the Ruddlesden-Popper phase $\text{Rb}_2\text{LaNb}_2\text{O}_7$ using rubidium metal.\textsuperscript{20} In many cases, the interlayer is the target of the topochemical manipulations but is not limited to only this area.
Substitution reactions targeting the actual perovskite layer are also possible as can be seen in the case of the superconducting Sr$_2$CuO$_2$F$_{2+6}$ obtained by treatment of Sr$_2$CuO$_3$ with F$_2$ gas where the oxygen on the BO$_6$ octahedra can be substituted for other anions.\textsuperscript{21} Substitution reactions can also be carried out on the A site in the perovskite slabs creating compounds that can have mixed A cation sites as in the case of KCa$_{2-x}$La$_x$Nb$_3$O$_{10}$\textsuperscript{22} However in this method the substitution is achieved using ceramic methods.

Solid state techniques can be long and tedious due to the required grinding and extended reactions times that can go from a couple of days to several weeks. In some instances, reaction times can be shortened to hours or even few minutes by using a molten flux method. Salt or eutectic mixtures such as Na$_2$SO$_4$-K$_2$SO$_4$\textsuperscript{23} can enhance the diffusion of the ions within the reagent mixture. The techniques have been delivering excellent results in the synthesis of pure compounds with control over the crystallite size of the products, and also the growth of single crystals.\textsuperscript{6}

It is possible to combine different topochemical techniques in order to obtain a specific compound, known as a multistep approach. This allows one to develop new structures that could eventually exhibit specific properties but that cannot be obtained by a single step reaction. Our group has been focusing on developing new multistep approaches for the creation of novel architectures in the layered perovskite interlayer spaces. For example, Choi et al. synthesized (A$_2$Cl)LaNb$_2$O$_7$ (A = Rb, Cs) by successive reductive and oxidative intercalation reactions on ALaNb$_2$O$_7$\textsuperscript{24} and Ranmohotti et al. were successful in building alkali-metal chalcogenide arrays between the perovskite slabs.\textsuperscript{25} Schaak and Mallouk reported the synthesis of three-dimensional perovskites through a multistep approach involving consecutive ion exchange and reductive deintercalation reactions on several series of both DJ and RP layered perovskites.\textsuperscript{26}
1.3 Characterization of Layered Perovskites

1.3.1 Crystal Structure

The most important aspect of each project described herein was the determination of the identity and structure of the compounds that were synthesized. Each solid consists of a regular arrangement of atoms in the three dimensions. This specific organization defines the crystal structure of the compound and can be represented in a given unit cell that is defined by the lattice parameters: the unit cell parameters a, b and c and the angles $\alpha$, $\beta$ and $\gamma$ as shown in Figure 1.4.

![Figure 1.4 Unit cell, lattice parameters and (122) plane](image)
Each unit cell is very specific to one compound as the atoms arrange themselves in a configuration that maximizes electrostatic interactions. Based on the different lattice parameters, a total of 7 crystal systems have been reported for the three-dimensional structures and the specific placement of the atoms in the unit cell that led to 14 possible variations, called Bravais lattices after French crystallographer August Bravais. Their description with respect to the lattice parameters is given in Table 1.1.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Coordinates Description</th>
<th>Unit Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>( a = b = c, \alpha = \beta = \gamma = 90^\circ )</td>
<td>P, F, I</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( a = b \neq c, \alpha = \beta = \gamma = 90^\circ )</td>
<td>P, I</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>( a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ )</td>
<td>P, F, I, A (B or C)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>( a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ )</td>
<td>P</td>
</tr>
<tr>
<td>Trigonal</td>
<td>(a) ( a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ )</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>(b) ( a = b = c, \alpha = \beta = \gamma \neq 90^\circ )</td>
<td>R</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>( a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ )</td>
<td>P, C</td>
</tr>
<tr>
<td>Triclinic</td>
<td>( a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ )</td>
<td>P</td>
</tr>
</tbody>
</table>

When describing a unit cell, people often refer to lattice planes that correspond to layers or sections within the unit cell, intercepting with different lattice points. Each plane is labeled using Miller indices \((hkl)\) derived for the reciprocal of the points at which the plane intercept the three axes of the unit cell. An example is given for the \((122)\) plane in Figure 1.4. In this case, the plane pictured in the unit cell cuts the three axes at 1, \( \frac{1}{2} \) and \( \frac{1}{2} \) for the \( a, b \) and \( c \) axes, respectively. The reciprocal of those fractions are 1, 2 and 2 which gives us the Miller indices \((122)\) of this plane.
1.3.2 X-ray diffraction

X-ray diffraction (XRD) is without any doubt the most widely used characterization technique in solid-state chemistry. This fingerprint technique is essential in phase recognition and for solving unknown crystal structures.

After production by means of a cathode X-ray tube (most commonly Cu or Mo), a monochromatic beam is focused on the sample and will interfere with the different atoms in the structure. Upon contact with the atoms, some of the beam will then be scattered by the atom’s electrons through elastic scattering. As mentioned before, atoms can be considered as ordered in specific lattice planes and the scattering of the X-ray beam by the atoms will produce constructive interference when Bragg’s law (Equation 1) is satisfied for planes separated by a specific distance “d” (Figure 1.5).

\[ 2d \sin \theta = n\lambda \]  

(1)

![Diagram of X-ray diffraction](image)

**Figure 1.5** Diffraction of X-rays by the atoms in a specific lattice plane
When the angle of incidence $\theta$ is other than one required to satisfy Bragg’s law, the reflected beams are out of phase leading to destructive interferences. The scattering power is directly related to the electron density of the compound. All elements will contribute to the scattering of the incident X-ray but heavier elements will diffract better than lighter ones.

As every crystalline compound has its own specific crystal structure and unit cell, the diffraction pattern is also going to be unique to that compound. Based on the arrangement of the atoms in the different lattice planes, the peaks positions will be directly associated with the $(hkl)$ Miller indices and the interlayer spacing can easily be derived from Bragg’s law. The unit cell parameters can then be calculated based on the interplanar d-spacing proper to each crystal system (Table 1.2).

**Table 1.2** Interlayer spacing formulae for the different crystal systems

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>d-spacing formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$\frac{1}{d^2} = \frac{1}{V^2} \left[ h^2 b^2 \sin^2 \alpha + k^2 a^2 c^2 \sin 2\beta + l^2 a^2 b^2 \sin 2\gamma + 2hkabc \left( \cos \alpha \cos \beta - \cos \gamma \right) + 2kla^2bc \left( \cos \beta \cos \gamma - \cos \alpha \right) + 2hlab^2c \left( \cos \alpha \cos \gamma - \cos \beta \right) \right]$</td>
</tr>
</tbody>
</table>
1.3.3 Magnetic Properties

One very interesting but challenging aspect of the characterization of solid state materials is the study of their magnetic behavior. All materials exhibit diamagnetism, where they repeal the magnetic field, but pure diamagnetism is only observed when all the electrons are paired. Unpaired electrons will cause the material to be attracted to the magnetic field. If unpaired electrons are randomly oriented in a material, this is referred as paramagnetism (Figure 1.6a). At certain temperatures, the spins in a paramagnetic material can eventually align to create ordered states in the sample. Spins orienting in a parallel manner create ferromagnetic interactions and an antiparallel orientation will lead to antiferromagnetic interactions. Figure 1.6 gives a simple representation of the different arrangements of the spins.

![Figure 1.6 Schematic representation of the spin orientation in (a) paramagnetic, (b) ferromagnetic and (c) antiferromagnetic materials](image)

More complex behavior can arise from the spin orientation. Disorder and frustration can lead to what are called spin glass transitions where both antiferromagnetic and ferromagnetic interactions are observed throughout the sample as the spins are frozen in a specific orientation. For example, the triple layered Li$_{0.3}$Ni$_{0.85}$La$_2$Ti$_3$O$_{10}$ reported by Neiner et al. exhibits two
magnetic transitions at low temperatures, from paramagnetic to ferromagnetic at 23 K and a spin glass transition at 10 K.27

Magnetic materials are characterized by their molar susceptibility and their unique temperature dependence. Ideal paramagnets follow the Curie law where the susceptibility varies inversely with the temperature:

\[ \chi = \frac{C}{T} \]

C is the Curie constant. Other types of paramagnetic materials can exhibit certain interactions which lead to a more complex behavior best described by the Curie-Weiss law:

\[ \chi = \frac{C}{T - \theta} \]

. The linear fit of the inverse susceptibility with the Curie-Weiss law allows one to obtain the value of the effective magnetic moment (\( \mu_{\text{eff}} \)) of the compound and the value of the Weiss constant (\( \theta \)). The \( \theta \) value gives important information concerning the type of interactions in the sample at lower temperatures. A positive Weiss constant indicates ferromagnetic interactions while a negative one is indicative of antiferromagnetic interactions; this is different from the simple Curie law where for ideal paramagnets, \( \theta = 0 \). Figure 1.7 shows a schematic representation of the linear inverse susceptibility depending on the type of interactions.
Figure 1.7 Inverse susceptibility as a function of temperature for an ideal paramagnet (black), a ferromagnet (red) and an antiferromagnet (blue)

As discussed previously, some compounds can be paramagnetic at high temperatures but eventually switch to another magnetic state at lower temperatures (ferromagnetic, antiferromagnetic or others). Magnetic transitions can be observed as a change in slope for the susceptibility as a function of the temperature. Figure 1.8 shows the temperature dependence of the susceptibility for paramagnetic, ferromagnetic and antiferromagnetic materials. In the case of a ferromagnet, one can observe a slow steady increase of the susceptibility as the temperature decreases and then at a certain point, critical temperature ($T_C$), there is a sharp susceptibility increase. In contrast, an antiferromagnet will initially exhibit a similar increase of the susceptibility on cooling and then at a certain temperature, the Néel point ($T_N$), the susceptibility will decrease.
Figure 1.8 Temperature dependence of the magnetic susceptibility for (a) paramagnetic, (b) ferromagnetic and (c) antiferromagnetic materials

1.4 References

Chapter 2

Thermally-Induced Layer Compression and Oxidative Deintercalation in Topochemically-Prepared, FeLa$_2$Ti$_3$O$_{10}$

2.1 Introduction

Topochemical manipulations have been extensively studied on layered perovskites to allow the formation of new compounds at low temperatures. The two main series, Dion-Jacobson (DJ) and Ruddlesden-Popper (RP) with general formula $A[A'_{n-1}B_nO_{3n+1}]$ and $A_2[A'_{n-1}B_nO_{3n+1}]$ (where $A$=alkali metal, $A'$=rare earth or alkaline-earth, $B$=transition metal, $n$=number of perovskite layers), respectively, have been proven to be very receptive to ion exchange of the interlayer alkali metal cations, $A$, present between the $[A'_{n-1}B_nO_{3n+1}]$ perovskite slabs. Ion exchanged compounds have received much interest due to their wide range of properties, including structural, magnetic or electronic ones. Monovalent and divalent ion-exchange as well as co-exchange reactions have been carried out on numerous DJ compounds to replace the alkali metal by smaller cations ($H^+$, $Li^+$, $Na^+$),$^1$ transition metal cations (in a 2-for-1 exchange)$^2,^3$ and MCl species ($M$= V, Cr, Mn, Fe, Co, Ni, Cu),$^4,^7$ respectively. In the case of RP compounds, monovalent ion exchange reactions were realized on Na$_2$La$_2$Ti$_3$O$_{10}$ to produce proton and lithium analogues, respectively using acid exchange$^8$ and molten salt reaction$^9$ with the corresponding nitrates. The alkali metal present in the interlayer of RP phases can also readily be replaced by a divalent ion such as Ca$^{2+},^10$ VO$^{2+},^11,^12$ and first row transition metals by different techniques such
as aqueous-solution reactions\textsuperscript{13} and solid-state reactions involving eutectic mixtures. The latter have been described by Hyeon and Byeon for the synthesis of M\textsuperscript{II}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} (M= Co, Cu, Zn).\textsuperscript{14}

The metastability of compounds obtained through topochemical manipulations often leads to decomposition of the layered perovskites at high temperatures into simpler structures.\textsuperscript{15} In contrast, phase transformations can sometimes be controlled to lead to new structures not obtainable by ceramic methods. Schaak and Mallouk for example were able to synthesize 3-D perovskites from layered compounds, such as CaEu\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10}, by heating the sample in hydrogen, reducing the perovskite slab (Eu\textsuperscript{3+} → Eu\textsuperscript{2+}), and leading to the formation of CaEu\textsubscript{2}Ti\textsubscript{3}O\textsubscript{9} with the deintercalation of water.\textsuperscript{3} A change in oxidation state, like shown here, can easily be induced using techniques like intercalation and deintercalation. The perovskite slab is usually where the change in oxidation state occurs, which in some instances can lead to mixed valency.\textsuperscript{16-18}

Simple thermal treatment of topochemically prepared compounds can also lead to new structures. Isothermal treatment of (CuCl)LaNb\textsubscript{2}O\textsubscript{7} under dynamic vacuum results in the deintercalation of cupric chloride to give Cu\textsubscript{0.5}LaNb\textsubscript{2}O\textsubscript{7}.\textsuperscript{2} In the case of KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}, a reversible transition from trigonal prismatic to cubic coordination for the interlayer potassium cation has been observed.\textsuperscript{19} Hyeon and Byeon reported an irreversible cell contraction in CuLa\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} upon heating up to 750 °C, consistent with a flattening of the MO\textsubscript{4} tetrahedra in the interlayer.\textsuperscript{14} Similar behavior was seen for Co and Zn analogues,\textsuperscript{14} though the extent of layer contraction was not as great.

In the work presented herein, we report the synthesis, structural characterization as well as the magnetic properties of the new DJ layered perovskite FeLa\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10}. Thermal studies show that the compound undergoes an unusual oxidative deintercalation to produce another phase,
Fe₀.₆₇La₂Ti₃O₁₀. As far we know, this is the first time that such a phenomenon is observed for the interlayer species in a layered perovskite.

### 2.2 Experimental

#### 2.2.1 Synthesis

\[ A₂La₂Ti₃O₁₀ \ (A = Li, Na) \] - Na₂La₂Ti₃O₁₀ was synthesized as reported in the literature.⁴ Stoichiometric amounts of La₂O₃ (Alfa Aesar, 99.99 %, dried at 1000 °C overnight to remove any hydroxides and carbonates) and TiO₂ (Alfa Aesar, 99.9 %) were ground with a 20 % molar excess of Na₂CO₃ (Alfa Aesar, 99.997 % anhydrous) to compensate for the loss of alkali metal oxide due to volatilization. The mixture was heated in an alumina crucible in a box furnace at 1050 °C for two days with two intermediate grindings. Li₂La₂Ti₃O₁₀ was synthesized through an ion exchange reaction as seen in the literature.⁹ Na₂La₂Ti₃O₁₀ and LiNO₃ (Alfa Aesar, 99%, anhydrous) were mixed together in a 1:10 molar ratio and placed in a combustion boat in a tube furnace for 12 hours at 300 °C. For both Na₂La₂Ti₃O₁₀ and Li₂La₂Ti₃O₁₀, after reaction the white products were washed with large amounts of DI-water, rinsed with acetone in a Büchner funnel, and then dried for 12 hours at 110 °C. Phase purity was verified for both starting materials by X-ray powder diffraction (XRD). The powder patterns were refined on tetragonal unit cells with \( a = 3.84(7) \ \text{Å} \), \( c = 28.560(6) \ \text{Å} \) and \( a = 3.8349(4) \ \text{Å}, \ c = 26.597(4) \ \text{Å} \) for Na₂La₂Ti₃O₁₀ and Li₂La₂Ti₃O₁₀, respectively; both cells are in agreement with the literature.⁹,²⁰

\[ FeLa₂Ti₃O₁₀ \] - FeLa₂Ti₃O₁₀ was synthesized through ion exchange. Li₂La₂Ti₃O₁₀ and FeCl₂ (Alfa Aesar, 99.5 % anhydrous), were ground together in a 1:2 molar ratio within an argon-filled glove box and pressed into pellets using a hand press. The pellets were heated under vacuum
(<10⁻⁴ Torr) in sealed Pyrex tubes at 350 °C for 5 days. After reaction, the brown sample was washed with DI-water in order to remove the excess iron chloride and the lithium chloride by-product, rinsed with acetone in a Büchner funnel, and dried overnight at 110 °C.

\(Fe_{0.67}La_2Ti_3O_{10}\) - The high-temperature phase was obtained by heating \(FeLa_2Ti_3O_{10}\) to 700 °C under constant argon flow in a tube furnace with a heating rate of 10 °C/min. In order to obtain a complete phase transformation, a 30 minute isotherm was carried out before the natural cooling of the sample to room temperature. The compound then appeared a dark reddish brown color due to the presence of the red \(\alpha-Fe_2O_3\) by-product. In an effort to remove the \(\alpha-Fe_2O_3\), the sample was washed with dilute HCl but a minor amount still remained in the sample after several washes.

High Pressure Treatment - High-pressure treatments were performed on both \(FeLa_2Ti_3O_{10}\) and \(Fe_{0.66}La_2Ti_3O_{10}\) using a cubic multianvil press. Each sample was loaded in a Pt cell and a pressure of 6 GPa was applied to the system at room temperature, 400, and 700 °C for 30 minutes.

2.2.2 Characterization

All compounds were characterized by X-ray powder diffraction (XRD) on a Philips X’Pert PW 3040 MPD system with a graphite monochromator (Cu Kα radiation, \(\lambda = 1.54056\) Å) with the exception of the high-pressure samples that were analyzed using a Mo source. The regular scans were collected in the range 3 – 75° 2θ in a continuous mode. The data used for structure refinement were collected in the range 5 – 110° 2θ. Lattice parameters were refined using Fullprof\(^{21}\) and Chekcell\(^{22}\) programs. Synchrotron XRD (SXRD) data were obtained on \(FeLa_2Ti_3O_{10}\) with a Debye–Scherrer camera at the BL02B2 beamline (\(\lambda = 0.42089\) Å) at SPring-
8 in Hyogo, Japan. Finely ground powder was inserted in a fused silica capillary tube (i.d. 0.5 mm) under inert atmosphere. The tube was continuously rotated during data acquisition to minimize the impact of any preferred orientation. High temperature scans, 10 minutes each, were also obtained at 200, 300, 400, 500, 600 and 700 °C.

Structure refinements for FeLa$_2$Ti$_3$O$_{10}$ (SXRD) and Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$ (XRD) were performed using JANA2006. Refined parameters include scale factor, zero-point shift, background, cell constants, atomic positions, peak shape and thermal parameters.

Stoichiometric compositions were examined by energy dispersive spectroscopy (EDS) on a JEOL JSM 5410 scanning electron microscope (SEM) equipped with an EDAX-DX Prime microanalytical system. All ratios were normalized to niobium. Only traces of alkali metal and chlorine were found in the ion-exchanged sample.

The $^{57}$Fe Mössbauer spectra were observed in transmission geometry in combination with a constant-acceleration spectrometer equipped with $^{57}$Co/Rh as the radiation source. $\alpha$-Fe was used as a control for velocity calibration and isomer shift. The obtained spectra were fit by a least-squares method with Lorentzian functions. Due to the small fraction of iron contained in the sample, one and two weeks of data acquisition was required to obtain decent statistics for FeLa$_2$Ti$_3$O$_{10}$ and Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$, respectively.

Thermal analysis was carried out by thermogravimetric/differential scanning calorimetry analysis (TGA/DSC) using a TA Instruments Thermal Analyst-2000. Measurements were performed in oxidizing and inert atmospheres between room temperature and 800 to 1000 °C by heating samples at 10 °C/min in O$_2$/Ar and Ar, respectively.

Magnetic measurements (ZFC/FC and hysteresis loops) were performed on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design,
in the temperature range of 4 K and 300 K in magnetic fields of 100, 500, 1000 and 5000 Oe. AC susceptibility measurements were carried out on a Quantum Design physical properties measurements system (PPMS) ac/dc magnetometer option with an ac drive field of 10 Oe and oscillating at 10, 100, 500, 1,000, 2,000, 5,000 and 10,000 Hz.

2.3 Results

2.3.1 Synthesis

\( \text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} \) readily undergoes ion exchange with iron chloride at low temperature for substitution of the alkali metals ions by Fe\(^{2+}\):

\[
\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} + \text{FeCl}_2 \rightarrow \text{FeLa}_2\text{Ti}_3\text{O}_{10} + 2 \text{LiCl} \quad (1)
\]

While the molar ratio of La and Ti remains 2 to 3 after ion exchange, the ratio of Fe was found to range from 0.9 to 1.0. The structural refinement presented below is consistent with a 1:2:3 ratio for Fe:La:Ti, respectively.

On heating FeLa\(_2\)Ti\(_3\)O\(_{10}\) in the presence of oxygen, the interlayer iron gets oxidized to form Fe\(_{0.67}\)La\(_2\)Ti\(_3\)O\(_{10}\) and a \( \alpha\)-Fe\(_2\)O\(_3\) (hematite) byproduct:

\[
2 \text{Fe}^{II}\text{La}_2\text{Ti}_3\text{O}_{10} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{Fe}_{0.67}^{III}\text{La}_2\text{Ti}_3\text{O}_{10} + \frac{1}{3} \text{Fe}_2\text{O}_3 \quad (2)
\]

This composition, \( x = 0.67 \) in Fe\(_x\)La\(_2\)Ti\(_3\)O\(_{10}\), is supported by TGA analysis under oxygen (see thermal behavior section) and Rietveld refinement data.

2.3.2 Structure

\( \text{FeLa}_2\text{Ti}_3\text{O}_{10}\). The ion exchanged product retains a layered structure similar to that of the parent, and is isostructural with previously reported CoLa\(_2\)Ti\(_3\)O\(_{10}\).\(^1\) XRD powder patterns of Li\(_2\)La\(_2\)Ti\(_3\)O\(_{10}\) and FeLa\(_2\)Ti\(_3\)O\(_{10}\), along with calculated CoLa\(_2\)Ti\(_3\)O\(_{10}\) are shown in Figure 2.1. The
synchrotron powder XRD pattern of the new iron phase was indexed on a tetragonal lattice with the refined cell parameters listed in Table 2.1.

![Graph showing X-ray diffraction patterns of different compounds]

**Figure 2.1** X-ray diffraction patterns of (a) Li<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>, (b) FeLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> and (c) calculated pattern of CoLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>.<sup>14</sup>

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt;La&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;10&lt;/sub&gt;</td>
<td>3.8349(4)</td>
<td>26.597(4)</td>
</tr>
<tr>
<td>FeLa&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;10&lt;/sub&gt;</td>
<td>3.81460(9)</td>
<td>27.2893(9)</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;0.67&lt;/sub&gt;La&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;10&lt;/sub&gt;</td>
<td>3.90281(9)</td>
<td>24.4834(8)</td>
</tr>
</tbody>
</table>

The CoLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> structural model with space group *I4/mmm* was used as a starting point for Rietveld refinement of the X-ray synchrotron data. Very minor reflections observed at 6.6, 7.3, 10.8 and 12.5 °2θ did not fit this model, and were therefore not included in the final refinement. A space group of lower symmetry may account for some of them. A peak asymmetry, was observed for all the 00ℓ reflections and any other peak with a large ℓ contribution. The
occupation factor for Fe was refined and confirmed the half occupancy of the tetrahedral site consistent with the 1:2:3 ratio for Fe:La:Ti and so was therefore set to 0.5 throughout the refinement. The thermal parameter of the oxygen sitting in the middle of the perovskite block (O2) remained high, even after moving the atom to the general positions (0,x,0) and investigating for a possible superstructure. The observed, calculated and difference plots for the Rietveld are shown in Figure 2.2. The atomic positions and selected bond lengths and angles are presented in Tables 2.2 and 2.3, respectively.

![Figure 2.2](image)

**Figure 2.2** Calculated (solid line), experimental (crosses) and difference (lower line) plots for the Rietveld refinement of FeLa$_2$Ti$_3$O$_{10}$ synchrotron data. Vertical tickmarks indicate individual reflections.
Table 2.2 Crystallographic Data for FeLa$_2$Ti$_3$O$_{10}$.

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>$g^a$</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$ (Å$^2$)</th>
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<tr>
<td>Fe</td>
<td>4d</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.0085(10)</td>
</tr>
<tr>
<td>La</td>
<td>4e</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.42100(4)</td>
<td>0.0057(3)</td>
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<tr>
<td>Ti1</td>
<td>2a</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0053(9)</td>
</tr>
<tr>
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<td>4e</td>
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<td>0</td>
<td>0</td>
<td>0.15572(9)</td>
<td>0.0017(7)</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
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<td>0</td>
<td>0</td>
<td>0.0710(4)</td>
<td>0.021(3)</td>
</tr>
<tr>
<td>O2</td>
<td>4c</td>
<td>1.0</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0.098(6)</td>
</tr>
<tr>
<td>O3</td>
<td>4e</td>
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<td>0</td>
<td>0</td>
<td>0.2230(3)</td>
<td>0.0021(2)</td>
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<tr>
<td>O4</td>
<td>8g</td>
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<td>0</td>
<td>0.5</td>
<td>0.1428(2)</td>
<td>0.009(2)</td>
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</table>

<table>
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<th>value</th>
</tr>
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<tr>
<td>space group</td>
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</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.81460(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>27.2893(9)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>397.09</td>
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<tr>
<td>$R_p$ (%)</td>
<td>7.00</td>
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<tr>
<td>w$R_p$ (%)</td>
<td>9.45</td>
</tr>
<tr>
<td>GOF</td>
<td>4.00</td>
</tr>
</tbody>
</table>

$^a$ g = occupancy

Table 2.3 Selected bond Lengths (Å) and Angles (°) for FeLa$_2$Ti$_3$O$_{10}$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O3 (x4)</td>
<td>2.04545(8)</td>
</tr>
<tr>
<td>Fe-O4 (x2)</td>
<td>2.9247(2)</td>
</tr>
<tr>
<td>Ti1-O1 (x2)</td>
<td>1.94022(7)</td>
</tr>
<tr>
<td>Ti1-O2 (x4)</td>
<td>1.90733(9)</td>
</tr>
<tr>
<td>Ti2-O1 (x1)</td>
<td>2.30939(8)</td>
</tr>
<tr>
<td>Ti2-O3 (x1)</td>
<td>1.84550(1)</td>
</tr>
<tr>
<td>Ti2-O4 (x4)</td>
<td>1.93884(9)</td>
</tr>
<tr>
<td>La-O1 (x4)</td>
<td>2.70594(5)</td>
</tr>
<tr>
<td>La-O2 (x4)</td>
<td>2.87841(7)</td>
</tr>
<tr>
<td>La-O4 (x4)</td>
<td>2.58346(6)</td>
</tr>
<tr>
<td>O3-Fe-O3</td>
<td>137.551(1)°</td>
</tr>
<tr>
<td>O3-Fe-O3</td>
<td>97.531(1)°</td>
</tr>
</tbody>
</table>
**Fe<sub>0.67</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>**. The diffraction pattern of the high temperature phase is very similar to that of La<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub><sup>21</sup> and shows evidence for the presence of α-Fe<sub>2</sub>O<sub>3</sub>. This latter component is consistent with the red particles observed in the sample after heating. FESEM images were taken to look at the morphology of Fe<sub>0.67</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> in comparison with the parent compound FeLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (Figure 2.3). As can be seen, the plate-like morphology of the crystallites is maintained after oxidative deintercalation of the iron oxide.

![FESEM picture of FeLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (left) and Fe0.67La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (right)](image)

**Figure 2.3** FESEM picture of FeLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (left) and Fe0.67La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (right)

The low angle reflections indicate that the layered structure is maintained at higher temperatures but the shift towards higher angles is a sign that the unit cell underwent a significant decrease along the c axis. Comparable thermally-induced layer contraction behavior was reported for the MLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub> (M = Co, Cu, Zn) compounds.<sup>14</sup> The pattern was indexed on a tetragonal phase similar to that of FeLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>. Unit cell parameters are shown in Table 2.1. Rietveld refinement was performed starting from the previous model. The presence of hematite in the sample after reaction was taken into consideration and included in the refinement. The iron occupancy was refined and the 0.31(1) value obtained is close to the expected 0.33. Due to their high instability, the thermal parameters were all fixed at 0.01. The proposed structure for this compound is presented in Figure 2.4 in comparison to that of FeLa<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>. Tables 2.4 and 2.5 list
the crystallographic data and selected bond lengths and angles, respectively, and the observed, calculated and difference plots for the Rietveld refinement are shown in Figure 2.5.

**Figure 2.4** (a) Structures of FeLa$_2$Ti$_3$O$_{10}$ (left) and Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$ (right). (b) Corresponding distorted interlayer FeO$_6$ octahedra.
**Table 2.4** Crystallographic Data for Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$.

<table>
<thead>
<tr>
<th>atom</th>
<th>g$^a$</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{iso}$ (Å$^2$)$^b$</th>
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<tr>
<td>Fe</td>
<td>0.31(1)</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.01</td>
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<tr>
<td>La</td>
<td>1.0</td>
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<td>0</td>
<td>0.4155(1)</td>
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</tr>
<tr>
<td>Ti1</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
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<tr>
<td>Ti2</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.1624(3)</td>
<td>0.01</td>
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<tr>
<td>O1</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.0718(9)</td>
<td>0.01</td>
</tr>
<tr>
<td>O2</td>
<td>1.0</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>O3</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.2305(9)</td>
<td>0.01</td>
</tr>
<tr>
<td>O4</td>
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<td>0</td>
<td>0.5</td>
<td>0.1604(9)</td>
<td>0.01</td>
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<table>
<thead>
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<th>value</th>
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<tr>
<td>a (Å)</td>
<td>3.9016(3)</td>
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<tr>
<td>c (Å)</td>
<td>24.466(2)</td>
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<tr>
<td>V (Å$^3$)</td>
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<tr>
<td>R$_p$ (%)</td>
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<tr>
<td>wR$_p$ (%)</td>
<td>15.16</td>
</tr>
<tr>
<td>GOF</td>
<td>1.71</td>
</tr>
</tbody>
</table>

$^a$ g = occupancy  
$^b$ fixed during the refinement

**Table 2.5** Bond Lengths (Å) and Angles (°) for Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Angle (°)</th>
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</thead>
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<tr>
<td>Fe-O3 (x4)</td>
<td>2.008(5) Å</td>
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<td>Fe-O4 (x2)</td>
<td>2.19(2)</td>
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<tr>
<td>Ti1-O1 (x2)</td>
<td>1.76(2)</td>
</tr>
<tr>
<td>Ti1-O2 (x4)</td>
<td>1.9508(3)</td>
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<tr>
<td>Ti2-O1 (x1)</td>
<td>2.21(2)</td>
</tr>
<tr>
<td>Ti2-O3 (x1)</td>
<td>1.67(2)</td>
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<td>Ti2-O4 (x4)</td>
<td>1.9514(6)</td>
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<tr>
<td>La-O1 (x4)</td>
<td>2.776(3)</td>
</tr>
<tr>
<td>La-O2 (x4)</td>
<td>2.843(2)</td>
</tr>
<tr>
<td>La-O4 (x4)</td>
<td>2.69(2)</td>
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<td>O3-Fe-O3</td>
<td>152.5(8)$^a$</td>
</tr>
<tr>
<td>O3-Fe-O3</td>
<td>93.2(2)</td>
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<td>O4-Fe-O3</td>
<td>103.7(6)</td>
</tr>
<tr>
<td>O4-Fe-O3</td>
<td>76.3(6)</td>
</tr>
</tbody>
</table>
2.3.3 Thermal Behavior

Thermal studies were carried at different temperatures on FeLa_2Ti_3O_10 under inert, oxidizing, and reducing atmospheres. Heating under inert atmosphere up to 700 °C in a sealed tube led to an important loss of crystallinity but no apparent decomposition as shown in the synchrotron data presented in Figure 2.6.
In the presence of oxygen, TGA results (Figure 2.7) show an initial weight loss corresponding to surface water, followed by a slight weight gain starting at 220 °C, reaching a plateau at 650 °C, and then maintaining the weight until the end of the run at 1000 °C. The weight uptake is consistent with the absorption of half a mole of oxygen to form Fe\(^{3+}\) as described in equation (2). DSC data shows no sharp exotherm but rather exhibits a slope change around 675 °C.
To better follow the oxidation of FeLa$_2$Ti$_3$O$_{10}$, a series of samples were individually heated to different temperatures up to 1000 °C in 100 °C steps. The treatment was carried out in a slightly oxidizing atmosphere (oxygen with argon). XRD patterns of each of the samples are shown in Figure 2.8. The initial change in the patterns was observed at 300 °C when the (110) reflection (33.5 °2θ) disappeared, possibly merging with the (017) reflection (initially at 33.1 °2θ). As the temperature was further increased, a distinct loss in crystallinity was observed until 600 °C. The significant peak broadening due to poor crystallinity contrasts with the pattern at 700 °C that shows very sharp well defined peaks of the new crystalline phase, Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$. 

Figure 2.7 Thermal analysis for FeLa$_2$Ti$_3$O$_{10}$, TGA (black, left) and DSC (blue, right) under Ar-O$_2$. 

![Thermal analysis graph](image)
Figure 2.8 Comparison of the XRD patterns of (a) FeLa\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} with the products annealed under Ar in the presence of oxygen at (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C, (f) 500 °C, (g) 600 °C, (h) 700 °C, (i) 800 °C, (j) 900 °C and (k) 1000 °C.

Detailed XRD studies from 600 to 700 °C (Figure 2.9) highlight the need for temperatures higher than 700 °C to obtain the Fe\textsuperscript{3+} phase. Elemental analysis on the washed sample showed little variation in iron content relative to FeLa\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10}. The layered compound remains stable up to 900 °C but collapses at 1000 °C to yield what appears to be a defective perovskite phase, possibly La\textsubscript{2/3}TiO\textsubscript{3} or an isostructural compound.
Figure 2.9 XRD pattern of (a) FeLa$_2$Ti$_3$O$_{10}$ sample after heating under constant Ar flow at (b) 675 °C for 30 min, (c) 700 °C without plateau, (d) 700 °C for 30 min and (e) 700 °C for 2h.

Thermal analysis was also conducted under reductive atmosphere (H$_2$). The resulting curve is presented in Figure 2.10, showing a very different behavior than that observed under O$_2$. No distinct thermal event was observed on the DSC curve. However the TGA data presents an interesting, reversible, small weight uptake starting at 220 °C, reaching a maximum around 430 °C and going down to finally reach a plateau around 600 °C. A sharp, sudden weight loss is observed at 850 °C. XRD analysis of the resulting compound after heating up to 1000 °C shows a mixture of La$_{2/3}$TiO$_3$ and La$_2$Ti$_2$O$_7$ along with an unidentified phase; these results are different from those obtained when conducting the same experiment under oxidative atmosphere, that resulted in only La$_{2/3}$TiO$_3$ (Figure 2.11). It is important to note that when the heating was
stopped at 800°C, right before the weight loss, the XRD pattern shows the same pattern as that of FeLa$_2$Ti$_3$O$_{10}$.

**Figure 2.10** TGA data for FeLa$_2$Ti$_3$O$_{10}$ under H$_2$-Ar.

**Figure 2.11** XRD of (a) FeLa$_2$Ti$_3$O$_{10}$ after heating at (b) 800 °C under H$_2$-Ar, (c) 1000 °C under H$_2$-Ar, (d) 1000 °C under O$_2$-Ar.
Particular attention was given to weight gain under dilute hydrogen. Isotherms (12 hours) were carried out at 340 and 400 °C to study the maximum mass intake as well as any possible structural change. It appears that the maximum weight gain of H₂, or possibly O₂, is similar at both temperatures (0.3-0.45%) but the curves are slightly different (Figure 2.12). After a sharp weight uptake, heating at 340 °C exhibits a constant, small, weight uptake for the majority of the time period. In contrast, heating at 400 °C shows a maximum weight gain after 3-4 hours followed by a weight loss and finally a plateau after 9 hours of the isotherm. It looks like that weight does not remain the same but rather oscillates, constantly going up and down. XRD for both samples show a similar pattern as that of the starting material with a slight shift of the first peaks to higher angles along with loss of (110) reflection at 33 °2θ. Additional attempts were made to isolate the compound at 430 °C but were unsuccessful as a weight loss was always observed upon cooling.

**Figure 2.12** TGA data for 12h isotherms under H₂-Ar at (a) 340 °C and (b) 400 °C
2.3.4 Mössbauer Spectroscopy

*FeLa₂Ti₃O₁₀* - The oxidation state of the iron atoms was confirmed to be +2 by Mössbauer spectroscopy. (Data collected by Mr. Yoshiteru Hosaka at Kyoto University.) The observed spectrum contains a magnetic doublet, pictured in Figure 2.13a, with an isomer shift (IS) of 0.96 mm/s and a quadrupole splitting (QS) of 1.79 mm/s, which is typical for Fe²⁺ in a tetrahedral coordination.²² This is consistent with the proposed structure obtained from the refinement.

![Mössbauer spectra](image)

**Figure 2.13** Mössbauer spectra of (a) FeLa₂Ti₃O₁₀ and (b) Fe₀.₆₇La₂Ti₃O₁₀. The circles are observed data and the spectra are fitted with (a) a magnetically ordered doublet and (b) magnetic ordered sextets of Fe₂O₃ and doublet for another Fe³⁺ ion.
$Fe_{0.67}La_2Ti_3O_{10}$. The presence of Fe$_2$O$_3$ in the high temperature phase was confirmed with the observance of a magnetically ordered sextet in the room temperature Mössbauer spectra (Figure 2.13b) with values of IS and QS in agreement with the referenced values for α-Fe$_2$O$_3${superscript 24} (Table 2.6). Another iron phase was also detected in the form of a doublet, where the IS and QS values are consistent with another type Fe$^{3+}$ ion in the sample, though whether the coordination of the species was tetrahedral or octahedral remained unclear. The relative difference in intensity for the two peaks of the doublet could possibly result from noise or some contribution from α-Fe$_2$O$_3$.

### Table 2.6 Fitting results of Mossbauer Spectra for FeLa$_2$Ti$_3$O$_{10}$ and Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$.

<table>
<thead>
<tr>
<th>Component</th>
<th>Isomer Shift (mm/s)</th>
<th>Quadrupole Splitting (mm/s)</th>
<th>Hyper Fine (T)</th>
<th>Area Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeLa$_2$Ti$<em>3$O$</em>{10}$</td>
<td>Doublet</td>
<td>0.96</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>Fe$_{0.67}$La$_2$Ti$<em>3$O$</em>{10}$</td>
<td>Doublet</td>
<td>0.38</td>
<td>0.91</td>
<td>70%</td>
</tr>
<tr>
<td>Sextet (Fe$_2$O$_3${superscript 25})</td>
<td>0.32 (0.38)</td>
<td>-0.28 (-0.2)</td>
<td>51.0 (52)</td>
<td>30%</td>
</tr>
</tbody>
</table>

1.1.1 Magnetic Behavior

$FeLa_2Ti_3O_{10}$. Temperature dependent magnetic susceptibility data in a 100 Oe field were collected on FeLa$_2$Ti$_3$O$_{10}$ and are shown in Figure 2.14a. The $\chi$ vs $T$ plot suggests antiferromagnetic-like behavior at lower temperatures, exhibiting a transition at 21 K. The magnetic response of the sample does not differ when the applied field is increased to 500 or 5000 Oe (Figure 2.15). A linear fit of the reciprocal susceptibility versus temperature was possible from 175 to 300 K (see inset Figure 2.14a), consistent with Curie-Weiss paramagnetism. The calculated moment for FeLa$_2$Ti$_3$O$_{10}$ of $\mu = 6.1 - 6.4$ μB is higher than the theoretical value of 4.90 μB expected for Fe$^{2+}$ in a high spin configuration.{superscript 26} The Weiss constant ($\theta$) of - 295 K further validates the existence of strong antiferromagnetic interactions at low temperatures.
Figure 2.14b shows the presence of a hysteresis below the transition, above this temperature, the hysteresis is no longer observed.

Figure 2.14 (a) Magnetic susceptibility vs T in a 100 Oe field. ZFC is shown as full circles and FC as open ones. Inset shows the linear reciprocal susceptibility vs T for 175 – 300 K (b) Hysteresis loops at 4, 23, 90 and 300 K. Inset shows the results for an applied field going from -50,000 to 50,000 Oe
Figure 2.15 Magnetic susceptibility at 100 (black) 500 (purple) 1000 (blue) and 5000 Oe (green). Transitions at 22.8, 21.8, 20.1 and 19.1 K for 100, 500, 1000 and 5000 Oe field, respectively.

One can observe the FC curve split from the ZFC curve at about 25 K. AC measurements were carried out in order to determine whether or not the event might be associated spin-glass transition (Figure 2.16). AC susceptibility at different frequencies ranging from 10 to 10,000 Hz show peaks for both the imaginary and real part, coinciding with the transition seen in the DC measurements. These set of peaks gradually shift to higher temperatures (25 to 30 K) with increasing frequency, characteristic of a spin-glass material.\(^{27}\)
Figure 2.16 AC susceptibility of FeLa$_2$Ti$_3$O$_{10}$ at 100 Oe for (a) real component ($\chi'$) at 10, 100, 500, 1000, 2000, 5000 and 10000 Hz (from left to right) and (b) imaginary component ($\chi''$) at 100, 500, 1000, 2000, 5000 and 10000 Hz (left to right).

$Fe_{0.67}La_2Ti_3O_{10}$. Magnetic measurements have been performed on the high temperature phase and are presented in Figure 2.17. Even though the $Fe_{0.67}La_2Ti_3O_{10}$ sample contains the $\alpha$-Fe$_2$O$_3$ byproduct, it is still possible to gleam some useful information from the magnetic analysis of this mixture. Initial results show a different behavior than that of FeLa$_2$Ti$_3$O$_{10}$ where the transition at around 25 K is no longer observed. However, the ZFC and FC curves splitting early on has been reported as magnetic behavior for the hematite, $\alpha$-Fe$_2$O$_3$, as the Morin transition of the oxide making it impossible to draw conclusions on the magnetic behavior of the new iron layered oxide. This further highlights the importance of obtaining a pure sample in order to draw any conclusion with respect to the magnetic behavior of the high temperature phase.
2.3.5 High Pressure behavior

Following the discovery of the cell contraction of FeLa$_2$Ti$_3$O$_{10}$, experiments were carried out to study the behavior of the compounds under high pressure at different temperatures. The XRD patterns of the resulting products presented in Figure 2.18 show that applying 6 GPa on FeLa$_2$Ti$_3$O$_{10}$ at room temperature and 400 °C lead to an important loss of crystallinity but the overall pattern remained the same. Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$ remained the same under high-pressure experiments on the compound at room temperature and 700 °C. Here also one can see the loss of crystallinity of the compound after experiment but no new reflections are observed.

Figure 2.17 ZFC-FC curves for Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$ at (a) 100, (b) 500, (c) 1000 and (d) 5000 Oe
Figure 2.18 XRD patterns of high pressure samples at 6 GPa of FeLa$_2$Ti$_3$O$_{10}$ at (a) 25°C, (b) 400°C and Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$ (c) at 25°C (red) and 700°C (green) (b and c were collected using a Mo X-ray source)

2.4 Discussion

A single-step topochemical reaction was used to obtain FeLa$_2$Ti$_3$O$_{10}$ from different analogues of the A$_2$La$_2$Ti$_3$O$_{10}$ series (A= alkali metals). While the reaction also occurs with Na and K, the use of the Li cation shortens the reaction time to 5 days versus the 14 days necessary for the ion exchange to be complete with the others. A similar decrease in reaction time had already been observed in reactions with Dion-Jacobson compounds, such in the formation of (FeCl)LaNb$_2$O$_7$ from ALaNb$_2$O$_7$ (A= alkali metals). The complete exchange of alkali metals for iron was
observed. This was supported by the elemental analysis, 1:2:3 for Fe:La:Ti, thermal analysis, as well as by the structure refinement data.

Previous attempts to synthesize FeLa$_2$Ti$_3$O$_{10}$ were reported by Hyeon and Byeon,$^{14}$ using molten salt reactions. These were limited by the formation of Fe$_2$O$_3$ as major impurity phase, which was not the case here. Their technique however was successfully applied to other M$^{II}$La$_2$Ti$_3$O$_{10}$ layered perovskites (M = Cu and Zn). Both the copper and zinc analogues can also be obtained using our same reaction approach. Based on the fact that both copper and iron compounds can be obtained at the same temperatures, efforts were made to combine both metals in the interlayer. The initials results are presented in Appendix 1.

The structure of FeLa$_2$Ti$_3$O$_{10}$ is comparable to the rest of the M$^{II}$La$_2$Ti$_3$O$_{10}$ series, with the transition metal sitting in a highly distorted tetrahedral site between the [La$_2$Ti$_3$O$_{10}$] perovskite layers. The unit cell expanded upon ion exchange despite the fact that Fe occupies only 50 % of the tetrahedral sites in the interlayer. Similar expansion was observed for the nickel exchanged compound.$^{13}$ The structure refinement was limited by the high thermal parameters for the oxygen atom sitting in the center of the perovskite slab (O2). While the tetragonal unit cell gives good results, the fit could possibly be improved by including a tilting of the octahedra in the perovskite slabs and/or the use a lower symmetry space group as in LiCa$_2$Nb$_3$O$_{10}$.$^{26}$ A lower symmetry model is currently under investigation.

Interestingly, the newly-synthesized compound undergoes unique chemical and structural changes at high temperatures. From 200 °C to 400 °C, the XRD pattern exhibits a “merging” of the 017 and 110 reflections, consistent with a contraction of the overall structure along the c axis, as well as a loss of crystallinity. Above 650 °C, the peaks corresponding to the new phase emerge and become more defined with time and higher temperatures until the high-temperature
(HT) phase becomes predominant in the sample. The transformation, occurring throughout a fairly large temperature range, allows one to witness the presence of both phases in the sample while heating (Figure 2.6). Time dependence studies showed that if the HT structure is dominant in a given sample at 700 °C, isothermal treatment at this temperature is necessary for the completion of the structural transformation. The remarkable stability of this phase up to 900 °C is in contrast with the thermal behavior of compounds observed in other topochemically prepared compounds that often decompose well below 800 °C; this greater stability opens the possibility of subsequent topochemical manipulations on this phase.

The XRD pattern of the resulting HT phase is very similar to that of the anion-deficient La$_2$Ti$_3$O$_9$ reported by Gönen et al. Refinement performed based on the FeLa$_2$Ti$_3$O$_{10}$ model shows the same contraction of the structure, with the very noticeable flattening of the central TiO$_6$ octahedra in the perovskite slab. The compression along the unit cell brings the perovskite slabs closer together modifying the environment of the iron atom towards a distorted octahedral coordination. No other report has been found relating this type of structural change for layered perovskites.

The formation of Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$ from FeLa$_2$Ti$_3$O$_{10}$ occurs through oxidative deintercalation in the presence of oxygen as seen in the TGA characterization. Oxygen is needed to convert the Fe(II) to Fe(III). To maintain charge balance with the perovskite slab, iron is deintercalated to produce Fe$_2$O$_3$ on the surface of the perovskite. It is expected that as oxygen contacts the surface of the perovskite, there is the simultaneous oxidation of iron within the perovskite slabs and deintercalation of iron with formation of the iron oxide. This would be consistent with the experiments carried out under high argon flow where the bulk of the sample turned dark brown and only the surface showed red particles (α-Fe$_2$O$_3$). Interestingly, this
reaction seems to be extremely favored as it occurs at even low partial pressures of oxygen. Reductive deintercalation followed by a structural rearrangement was previously observed by Schaak and Malouk with the synthesis of 3-D perovskites from RP precursors. In their case the Eu in the perovskite slabs were reduced in hydrogen upon heating, leading to the formation of perovskites $A^{II}\text{Eu}_2\text{Ti}_3\text{O}_9$ and $M^{II}\text{Eu}_2\text{Ti}_3\text{O}_9$ ($A^{II} = \text{Ca, Sr}$; $M^{II} = \text{Ni, Cu, Zn}$).

Mossbauer spectroscopy was an important tool in understanding the behavior of $\text{FeLa}_2\text{Ti}_3\text{O}_{10}$. It confirmed the +2 oxidation state of the iron atoms as well as their coordination in the interlayer. Additionally it showed clear evidence for a change in oxidation state from +2 to +3 after heating. The characterization results are consistent with the presence of hematite, $\alpha$-$\text{Fe}_2\text{O}_3$, in the sample along with another type of iron atom. It appears that the second Fe$^{3+}$ ions, whose charge has been established according to the IS of 0.38, still lie in a similar site to that of the parent compound, based on the QS of 0.91. The decrease in the value of the QS, however, indicates a decrease in surrounding asymmetric electric charge distribution, consistent with the proposed structure. Indeed, the contraction of the unit cell leads to a decrease in interlayer space, bringing the oxygen atoms from opposite perovskite slabs closer to each other as well as the interlayer iron atoms forming what one can consider a highly distorted octahedron (Figure 2.4b).

In order to maintain the overall charge neutrality, the resulting compound is expected to be $\text{Fe}_{0.67}\text{La}_2\text{Ti}_3\text{O}_{10}$. The structure refinement supported this with a resulting formula of $\text{Fe}_{0.61}\text{La}_2\text{Ti}_3\text{O}_{10}$; additionally, the Mossbauer data show 30:70 ratio for the $\text{Fe}_2\text{O}_3$:HT Phase iron content in the unwashed sample. Results from the bond valence sum (BVS) calculations presented in Table 2.7 are also consistent with expected values for Fe$^{2+}$ and Fe$^{3+}$ in the LT and HT phases, respectively.
Table 2.7 Bond valence sums (BVS) for FeLa$_2$Ti$_3$O$_{10}$ and Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$

<table>
<thead>
<tr>
<th></th>
<th>FeLa$_2$Ti$<em>3$O$</em>{10}$</th>
<th>Fe$_{0.67}$La$_2$Ti$<em>3$O$</em>{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td>La</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Ti</td>
<td>3.9</td>
<td>4.2</td>
</tr>
</tbody>
</table>

The magnetic behavior of FeLa$_2$Ti$_3$O$_{10}$ resembles that of Li$_{0.31}$Ni$_{0.85}$La$_2$Ti$_3$O$_{10}$

$^{13}$ ZFC/FC curves split below 25 K, in a similar manner to other spin glasses. A spin glass is a highly disordered magnet containing both ferromagnetic and antiferromagnetic bonds which results in a magnetically frustrated state. With the filling of only half of the tetrahedral sites by Fe$^{2+}$ it is possible a clear ordering of the spins might not be possible leading a disordered state. The magnetic moment calculated from the linear fit of the reciprocal susceptibility is higher than that expected for Fe$^{2+}$ ions in the high spin state. Such behavior has already been observed by Parks and Akhtar in different Fe$^{2+}$ containing magnetic materials.$^{29}$ The close distance (~2.7 Å) between adjacent iron atoms could be responsible for an exchange type interaction that may result in a larger effective moment.

2.5 Conclusions

A new layered perovskite, FeLa$_2$Ti$_3$O$_{10}$, was prepared by ion exchange of the triple-layered Ruddlesden-Popper phase Li$_2$La$_2$Ti$_3$O$_{10}$ and FeCl$_2$ at 350 °C under static vacuum. Magnetic measurements on FeLa$_2$Ti$_3$O$_{10}$ display Curie-Weiss behavior at high temperatures with a magnetic moment larger than typically observed for high spin Fe$^{2+}$. At lower temperatures (< 30 K), a spin-glass transition is observed. Thermal analysis of the sample to 700 °C in the presence of oxygen shows that FeLa$_2$Ti$_3$O$_{10}$ undergoes a significant cell contraction ($\Delta c \approx 2.7$ Å) with a
change in the oxidation state of iron (Fe$^{2+}$ to Fe$^{3+}$) and deintercalation of iron as Fe$_2$O$_3$ to produce Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$. Structural analysis and Mössbauer studies indicate that on oxidation, the local iron environment goes from tetrahedral to a distorted octahedral coordination.

### 2.6 References

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Chapter 3


3.1 Introduction

Perovskites have received much interest due to their structural diversity and properties.\textsuperscript{1} The ability to vary the composition of different phases to form solid-solutions through atomic substitution at the A or B sites with ions of similar or different charge, can lead to new structures as well new properties or the enhancement of those of the original compound. In $La_1-xSr_xCoO_3$ for example, mixing of cationic A-sites has been extensively studied for metal-insulator transitions associated with multiple structural variations at different compositions.\textsuperscript{2} In $La_2CuO_4$, an insulator, A-site substitutions in $La_{2-x}A_xCuO_{4-x/2+δ}$ ($A = Nd, Bi$) solid-solutions has produced superconductivity.\textsuperscript{3} In another study, Gopalakrishnan et al. reported on variations in acidity based on A/B site substitution in $HCa_{2-x}La_xNb_3-xTi_xO_{10}$.\textsuperscript{4}

The Dion-Jacobson (DJ) and Ruddlesden-Popper (RP) series of layered perovskites have the general formula $A'[A_{n-1}B_nO_{3n+1}]$ and $A'_2[A_{n-1}B_nO_{3n+1}]$, respectively, where $A' =$ alkali metal, $A =$ rare earth or alkaline-earth, $B =$ transition metal, and $n =$ number of perovskite layers. Solid solutions can be obtained either by direct or multiple step reactions in the case of layered compounds ($n \geq 3$) such as $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$ and the ion exchange product $(CuCl)CaNa_2Nb_4O_{13}$.\textsuperscript{5,6} Substitution of the A cation for differently charged species allows for
mixed valency in the B cations as seen in KCa$_2$La$_x$Nb$_3$O$_{10}$; this in turn can lead to a change in the interlayer electron density. Bridging between the two families (DJ and RP), to create new solid solutions is another method to create mixed A site perovskite derivatives as was presented by Kim et al. with the synthesis of the Rb$_{2-x}$La$_x$Ti$_{3-x}$Nb$_x$O$_{10}$ solid-solution where $0.0 \leq x \leq 1.0$. In most cases, the atoms substituting the A site in the perovskite slabs differ in charge by only ±1. Very few reports of a bigger charge differences can be found in the literature.

Herein we present the synthesis and characterization of the new mixed A-cation containing layered perovskite RbLaNaNb$_3$O$_{10}$, where La$^{3+}$ and Na$^+$ share the same site in the perovskite slab. This compound is isostructural with RbCa$_2$Nb$_3$O$_{10}$. Further topochemical manipulation of this phase via ion exchange reactions at low temperatures (< 500 °C), lead to the new series A’LaNaNb$_3$O$_{10}$ where A’= H, Li, Na, K and CuCl. In this study, we focus on adding to the library of layered perovskites by not only creating a new compound, but by also showing its ability to further be manipulated, and by studying the stability of the series through thermal behavior studies. The new compounds seem to be isostructural with the known published series, A’Ca$_2$Nb$_3$O$_{10}$ where A’ is H, Li, Na, K, Rb, and CuCl.

### 3.2 Experimental

**3.2.1 Synthesis**

RbLaNaNb$_3$O$_{10}$ was prepared by ceramic method from Rb$_2$CO$_3$ (Alfa Aesar, 99%), La$_2$O$_3$ (Alfa Aesar, 99.99%), Na$_2$CO$_3$ (Alfa Aesar, 99.997% anhydrous), and Nb$_2$O$_5$ (Alfa Aesar, 99.9985%). La$_2$O$_3$ and Nb$_2$O$_5$ were heated to 1000°C for 24 h before reaction, to remove any hydroxides or carbonates as impurities. Stoichiometric amounts of the oxides along with 25%
excess of the carbonates were ground together and calcinated at 850 °C for 24 h in an alumina crucible, reground, and heated at 1150 °C for 24 h. Post reaction, the mixture was washed with hot distilled water in order to remove any unreacted carbonate, rinsed with acetone using suction filtration, followed by a drying step at 100 °C for 12 h. KLaNaNb$_3$O$_{10}$ was obtained by the same direct method with K$_2$CO$_3$ (Alfa Aesar, 99.9%).

Attempts were made to synthesize RbLaANb$_3$O$_{10}$ where A=Li and K through a two steps reaction. RbLaNb$_2$O$_7$ and ANbO$_3$ compounds were ground together in a 1:1 and heated at 1050-1150 °C for 12-48hrs. No evidence of formation of the targeted triple layered compounds was found in the XRD pattern. More details on the two step approach is given in Appendix 1.

Ion exchange reactions were conducted to obtain the new ALaNaNb$_3$O$_{10}$ series (A= H, Li, Na, K). RbLaNaNb$_3$O$_{10}$ was ground in a 1:10 molar ratio with LiNO$_3$ (Alfa Aesar, 99%), NaNO$_3$ (Alfa Aesar, 99.999%), KNO$_3$ (Alfa Aesar, 99.994%), and heated for 4 days at 350, 400 and 400 °C, respectively. The proton exchange reaction took place in 50 ml solution of 6 M HCl, stirred at 60 °C for 3 days. The solution was refreshed every day. The reaction was also carried out using 6M nitric acid but this resulted in a poorly crystalline compound. (CuCl)$_2$LaNaNb$_3$O$_{10}$ was synthesized by a method similar to that reported by Kodenkandath et al. RbLaNaNb$_3$O$_{10}$ and anhydrous CuCl$_2$ (Alfa Aesar, 99.995%) were mixed in an argon-filled glovebox in a 1:2 molar ratio, and finely homogenously ground using a mortar and pestle. The mixture was pressed into pellets using a hand press (Sigma Aldrich), sealed under vacuum in a Pyrex tube, and heated at 350 °C for 3 days. The various products were washed with copious amounts of hot water to remove unreacted starting material and rubidium by-products, rinsed with acetone, and dried overnight at 100 °C.
3.2.2 Characterization

All compounds were characterized by X-ray powder diffraction (XRD) using a Philips X’Pert PW 3040 MPD system with a graphite monochromator (Cu Kα radiation, λ = 1.54056 Å). The regular scans were collected in the range of 3 – 75 ° 2θ in continuous mode. Data used for structure refinement were collected in the range of 5 – 110 ° 2θ. Lattice parameters were refined using Fullprof\textsuperscript{13} and Chekcell\textsuperscript{14} programs.

Crystal structure refinement of RbLaNaNb\textsubscript{3}O\textsubscript{10} was carried out using the Rietveld technique with the GSAS program.\textsuperscript{15} Refined parameters include scale factor, zero-point shift, background, cell constants, atomic positions, and peak shape.

Stoichiometric compositions were examined by energy dispersive spectroscopy (EDS) on a JEOL JSM 5410 scanning electron microscope (SEM) equipped with an EDAX-DX Prime microanalytical system. All ratios were normalized to niobium.

Thermal analysis was carried out by thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) using a TA Instrument SDT Q600. Measurements were performed under flowing argon from room temperature to 1000 °C at a heating rate of 10 °C/min.

3.3 Results

RbLaNaNb\textsubscript{3}O\textsubscript{10} was successfully synthesized for the first time using the ceramic method. According to the XRD pattern, the resulting compound appears to be isostructural with RbCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}\textsuperscript{16} as pictured in Figure 3.1. Elemental analysis confirmed the composition to be 1.0(1): 1.3(9): 1.0(1): 3 for the Rb:La:Na:Nb ratio.
Figure 3.1 Powder X-ray diffraction patterns for (a) RbLaNaNb$_3$O$_{10}$ and (b) RbCa$_2$Nb$_3$O$_{10}$

All the peaks of the solid-solution were indexed on a tetragonal unit cell with P4/mmm space group in agreement with the reported structure of RbCa$_2$Nb$_3$O$_{10}$. Structural refinement was conducted by Rietveld methods. The starting model was based on that of the calcium analogue, where La and Na were constrained to share the Ca site at 50% occupation for both. While the model gave a very good fit with reasonable reliability factors, the thermal parameters of the rubidium as well as that of O1, the oxygen atom sitting in the middle of the perovskite layer, were significantly larger than that of the other atoms. Considering the slightly larger atomic radii of La$^{3+}$ (1.50 Å) and Na$^+$ (1.53 Å) compared to that of Ca$^{2+}$ (1.48 Å), it is possible that a certain distortion with regard to the original model might be present, leading to a less symmetrical system. Moving O1 to a more general position leads to a larger thermal parameter. Moreover, the local variations in charge between La$^{3+}$ and Na$^+$ could potentially induce tilting of the NbO$_6$ octahedra. Such behavior has been observed in double layered RbLaNb$_2$O$_7$. The observed,
calculated and difference plots for the Rietveld refinement are shown in Figure 3.2, the structural data in Table 3.1, selected bond distances in Table 3.2, and the final structure can be seen in Figure 3.3.

**Figure 3.2.** Calculated (solid line), experimental (crosses) and difference (lower line) plots for the Rietveld refinement of RbLaNaNb$_3$O$_{10}$
**Table 3.1** Crystallographic data for RbLaNaNb\textsubscript{3}O\textsubscript{10}

<table>
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<tr>
<th>atom</th>
<th>g *</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U\textsubscript{iso} (Å\textsuperscript{2})</th>
</tr>
</thead>
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<tr>
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<td>0.5</td>
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<td>0.0084(7)</td>
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<td>0.001(4)</td>
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- g = occupancy

<table>
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</tr>
<tr>
<td>c (Å)</td>
<td>15.1349(5)</td>
</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
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</tr>
<tr>
<td>R\textsubscript{p} (%)</td>
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<tr>
<td>wR\textsubscript{p} (%)</td>
<td>13.78</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>3.071</td>
</tr>
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</table>

**Table 3.2** Selected bond distances for RbLaNaNb\textsubscript{3}O\textsubscript{10}

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<tr>
<td>Rb - O4 (x8)</td>
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<tr>
<td>La/Na - O1 (x4)</td>
<td>2.932(2)</td>
</tr>
<tr>
<td>La/Na - O2 (x4)</td>
<td>2.764(2)</td>
</tr>
<tr>
<td>La/Na - O3 (x4)</td>
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</tr>
<tr>
<td>Nb1 - O1 (x4)</td>
<td>1.94351(3)</td>
</tr>
<tr>
<td>Nb1 - O2 (x2)</td>
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</tr>
<tr>
<td>Nb2 - O2 (x1)</td>
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</tr>
<tr>
<td>Nb2 - O3 (x4)</td>
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</tr>
<tr>
<td>Nb2 - O4 (x1)</td>
<td>1.77(1)</td>
</tr>
</tbody>
</table>
Figure 3.3 Structure of RbLaNaNb$_3$O$_{10}$

ALaNaNb$_3$O$_{10}$ (A=H, Li, Na and K) and (CuCl)LaNaNb$_3$O$_{10}$ were synthesized using ion exchange reactions on the rubidium compound by methods that have been developed in our group.$^{19}$ All the products, shown in Figure 3.4, were confirmed to be single phase according to the XRD and elemental analysis. Minimal traces of rubidium were found in some samples although never exceeding 3%. Based on XRD data, the new series is isostructural with the respective ACa$_2$Nb$_3$O$_{10}$ series (A=H, Li, Na, K and CuCl). The compounds were indexed in the tetragonal system and the unit cell parameters were compared to the corresponding Ca products (Table 3.3). Both the proton and sodium exchanged products form hydrates and the water content was determined using thermal gravimetric analysis. Preliminary structure refinement on the copper-chloride compound supports the phenomenon observed by Kodenkandath et al.$^{12}$ where
the Rb$^+$ interlayer cations are replaced by [CuCl]$^+$ entities forming square planar arrays, leading to a typical cell expansion of about 0.7 Å along the $c$ axis.

**Figure 3.4** XRD patterns of the ion exchange products: (a) HLaNaNb$_3$O$_{10}$•1.2H$_2$O, (b) LiLaNaNb$_3$O$_{10}$, (c) NaLaNaNb$_3$O$_{10}$, (d) NaLaNaNb$_3$O$_{10}$•2H$_2$O, (e) KLaNaNb$_3$O$_{10}$, (f) (CuCl)LaNaNb$_3$O$_{10}$

Thermal studies were carried out on all the ion exchanged products. LiLaNaNb$_3$O$_{10}$ and (CuCl)LaNaNb$_3$O$_{10}$ both decompose exothermically while HLaNaNb$_3$O$_{10}$ and NaLaNaNb$_3$O$_{10}$ only exhibit an endotherm during the dehydration process. KLaNaNb$_3$O$_{10}$, on the other hand, does not appear to decompose at all up to 1000 °C, which is further confirmed through XRD. The ALaNaNb$_3$O$_{10}$ compounds, where A= H, Li and Na, all decompose into the final products, LaNbO$_4$ and NaNbO$_3$ upon heating in addition of LiNbO$_3$ for the lithium analogue. While the
lithium structure decomposes exothermally in a single transition at 783 °C, the proton and sodium compounds proceed according to a multi-step decomposition pathway. First, endothermic dehydration is observed at 72 °C for H and 102 °C for Na; the

**Table 3.3** Refined unit cell parameters for the ALaNaNb$_3$O$_{10}$ series compared to the ACa$_2$Nb$_3$O$_{10}$ series

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Layer spacing (Å)</th>
</tr>
</thead>
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<tr>
<td>HLaNaNb$<em>3$O$</em>{10}$</td>
<td>3.87(4)</td>
<td>14.546(2)</td>
<td>217.85</td>
<td>14.54</td>
</tr>
<tr>
<td>HCa$_2$Nb$<em>3$O$</em>{10}$ &amp; 3.8536(6)</td>
<td>14.437(5)</td>
<td>213.89</td>
<td>14.40</td>
<td></td>
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<tr>
<td>HLaNaNb$<em>3$O$</em>{10}$•1.2H$_2$O</td>
<td>3.87(2)</td>
<td>16.310(2)</td>
<td>244.27</td>
<td>16.31</td>
</tr>
<tr>
<td>HCa$_2$Nb$<em>3$O$</em>{10}$•1.3H$_2$O &amp; 3.8565(6)</td>
<td>16.200(5)</td>
<td>240.94</td>
<td>16.20</td>
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</tr>
<tr>
<td>LiLaNaNb$<em>3$O$</em>{10}$</td>
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<tr>
<td>LiCa$_2$Nb$<em>3$O$</em>{10}$ &amp; 7.720(7)</td>
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<tr>
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<td>5.470(4)</td>
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<td>NaCa$_2$Nb$<em>3$O$</em>{10}$ &amp; 5.4731(2)</td>
<td>29.0138(9)</td>
<td>869.10</td>
<td>14.51</td>
<td></td>
</tr>
<tr>
<td>NaLaNaNb$<em>3$O$</em>{10}$•2H$_2$O</td>
<td>9.67(1)</td>
<td>16.880(1)</td>
<td>1578.43</td>
<td>16.88</td>
</tr>
<tr>
<td>NaCa$_2$Nb$<em>3$O$</em>{10}$•2H$_2$O &amp; N/A</td>
<td>16.832(1)</td>
<td>N/A</td>
<td>16.83</td>
<td></td>
</tr>
<tr>
<td>KLaNaNb$<em>3$O$</em>{10}$</td>
<td>7.768(7)</td>
<td>14.8865(3)</td>
<td>898.28</td>
<td>14.89</td>
</tr>
<tr>
<td>KCa$_2$Nb$<em>3$O$</em>{10}$ &amp; 7.741(5)</td>
<td>14.8611(8)</td>
<td>890.52</td>
<td>14.86</td>
<td></td>
</tr>
<tr>
<td>RbLaNaNb$<em>3$O$</em>{10}$</td>
<td>3.88703(7)</td>
<td>15.1349(5)</td>
<td>228.67</td>
<td>15.14</td>
</tr>
<tr>
<td>RbCa$_2$Nb$<em>3$O$</em>{10}$ &amp; 3.85865(6)</td>
<td>14.9108(3)</td>
<td>222.01</td>
<td>14.91</td>
<td></td>
</tr>
<tr>
<td>(CuCl)LaNaNb$<em>3$O$</em>{10}$</td>
<td>3.8803(3)</td>
<td>15.8571(1)</td>
<td>238.75</td>
<td>15.85</td>
</tr>
<tr>
<td>(CuCl)Ca$_2$Nb$<em>3$O$</em>{10}$ &amp; 3.8496(2)</td>
<td>15.6593(7)</td>
<td>232.06</td>
<td>15.65</td>
<td></td>
</tr>
</tbody>
</table>

weight decrease corresponds to the loss of 1.2 H$_2$O molecules (3.6 wt%) and 2 H$_2$O molecules (5 wt%) for H and Na, respectively. The dehydration step is correlated with the major shift of the first reflection to higher angles in the XRD pattern, consistent with the extraction of water molecules from the structure leading to a cell contraction along the c axis (Figure 3.4c,d). At 320
°C, HLaNaNb₃O₁₀ undergoes a second weight loss of 1.4 wt% centered at 335 °C. For further characterization, HLaNaNb₃O₁₀ was heated to 400 °C and allowed to cool down to room temperature. Figure 5 shows the XRD pattern of the hydrated protonated compound before TGA, the TGA products at 400 and 1000°C, and the decomposition products after heating at 1000°C. The resulting compound (Figure 3.5b) at 400 °C is somewhat similar to the experimental pattern of Ca₄Nb₆O₁₉ reported by Fang et al²³; the calculated pattern is presented in Figure 3.5d for comparison. This is consistent with a decomposition through a condensation step giving off water (theoretical 1.50 wt%); no distinct thermal event was observed. After heating to 1000 °C, the layered compound falls apart and decomposes into NaNbO₃ (Fig 3.5e), LaNbO₄ (Fig 3.5f), and Na₀.₅La₀.₅Nb₂O₆.

Figure 3.5 XRD patterns of (a) HLaNaNb₃O₁₀•1.2H₂O and the resulting TGA products at (b) 400 °C (c) 1000 °C compared with (d) Ca₄Nb₆O₁₉, (e)NaNbO₃ and (f) LaNbO₄
NaLaNaNb$_3$O$_{10}$ follows a similar pathway as its lithium analogue where it also forms LaNbO$_4$ (both monoclinic and tetragonal structures) and NaNbO$_3$. The XRD pattern of the decomposed TGA products showed remaining peaks from the starting material. The absence of a thermal event further indicates that the decomposition actually occurs over a large temperature range.

(CuCl)LaNaNb$_3$O$_{10}$ does not follow the same decomposition pathway that leads to the formation of simple perovskites. It undergoes three consecutive weight losses centered at 655, 780 and 860-865 °C under argon, as shown in Figure 3.6. CuCl, CuO and Na$_{0.5}$La$_{0.5}$Nb$_2$O$_6$ were identified as major phases through XRD data indicating that the first endothermic weigh loss is due to the removal of chlorine from the mixture. The second weight loss is not associated with any clear thermal event but rather a slope change. The mass of the sample plateaus out after the 7.7 % mass loss before decreasing again (0.5 wt%) to reach a final plateau up to the end of the

Figure 3.6 TGA (blue) and DSC (red) curves for (CuCl)LaNaNb$_3$O$_{10}$ under argon
measurement at 1000 °C. NaNbO₃ and LaNbO₄ as well as phases isostructural with Ca₂Nb₂O₇ and CaNb₂O₆ were identified as the final products (Figure 3.7). Some disparities in peak positions can be attributed to the difference in composition for the layered compounds. Elemental analysis shows remaining copper in the sample after 1000 °C but no evidence for any copper related compound has been found in the XRD pattern.

**Figure 3.7** (a) Final decomposition product for (CuCl)LaNaNb₃O₁₀ compared to references for (b) CaNb₂O₆, (c) CaNb₂O₇, (d) LaNbO₄, (e) NaNbO₃
3.4 Discussion

Triple layered RbLaNaNb$_3$O$_{10}$ was synthesized by the ceramic method. High temperatures, above 1100 °C, were used to prevent the formation of the double-layered phase RbLaNb$_2$O$_7$. It is one of the rare substituted layered perovskites with A cations having a charge difference higher than one. The new compound is isostructural with RbCa$_2$Nb$_3$O$_{10}$ (Figure 3.1). Charge neutrality and structural stability of the new solid-solution is achieved by the random distribution of La$^{3+}$ and Na$^+$ ions in the A site of the perovskite slab, whose random sharing of the site was confirmed by structure refinement. The new Rb compound exhibits the same type of very highly distorted NbO$_6$ octahedron as the calcium phase, typical of the second order Jahn-Teller effect observed in numerous layered perovskites.\(^{24}\) It appears that the comparable size of La$^{3+}$ and Na$^+$ plays an important role in the stability of the structure despite the charge difference between the two cations. Synthesis with monovalent cations smaller or bigger than La, Li, and K, respectively, were attempted at different temperatures but yielded the double layered RbLaNb$_2$O$_7$ and simple perovskites phases, with no evidence of the targeted triple layered product. The tolerance factors for Li and K in the A site of the perovskite are 0.85 and 1.09, respectively. While that of K is higher than one and therefore a stable perovskite structure is not expected, Li could well sit in a distorted perovskite structure. However, the big difference in size between cations sharing the same site may bring too much of a structure distortion in the perovskite slab for the compound to be stable.

Along with its high temperature stability, RbLaNaNb$_3$O$_{10}$ showed its ability to be manipulated using topochemistry with various metal nitrates and chlorides under mild conditions. A new series of Dion-Jacobson type triple layered perovskites, A’LaNaNb$_3$O$_{10}$ (A’=H, Li, Na, K) was obtained through exchange reactions with the corresponding nitrates.
(except the proton exchange) with RbLaNaNb₃O₁₀. (CuCl)LaNaNb₃O₁₀ was obtained by reaction with CuCl₂. Similar to the parent compound, the entire series is isostructural with A’Ca₂Nb₃O₁₀. An increase in unit cell parameters is observed in comparison to those of the corresponding calcium analogues which is consistent with the substitution of calcium for slightly bigger cations. Such behavior is commonly seen in solid solution compounds when different sized atoms share a common site in the perovskite slab. The c parameter increases as is indicated by the shift to lower angles of the first reflection through XRD data, going from H to Rb compounds (Table 3.3 and Figure 3.4). This trend is consistent with the increasing size of the cations as you go down the alkali metal group.

TGA and DSC data were collected in order to determine the thermal stability of the new ion exchanged products. Suggested decomposition pathways are presented in Table 3.4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>DSC</th>
<th>Decomposition Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLaNaNb₃O₁₀</td>
<td>No distinct thermal event</td>
<td>2 HLaNaNb₃O₁₀  \rightarrow  &quot;(LaNa)₂Nb₆O₁₉&quot; + H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(LaNa)₂Nb₆O₁₉  \rightarrow  LaNbO₄ + NaNbO₃ + 2 Na₀.₅La₀.₅Nb₂O₆</td>
</tr>
<tr>
<td>LiLaNaNb₃O₁₀</td>
<td>Exotherm 783 °C</td>
<td>LiLaNaNb₃O₁₀  \rightarrow  LiNbO₃ + NaNbO₃ + LaNbO₄</td>
</tr>
<tr>
<td>NaLaNaNb₃O₁₀</td>
<td>No distinct thermal event</td>
<td>NaLaNaNb₃O₁₀  \rightarrow  2 NaNbO₃ + LaNbO₄</td>
</tr>
<tr>
<td></td>
<td>Endotherm 657 °C</td>
<td>(CuCl)LaNaNb₃O₁₀  \rightarrow  Cl₂ + CuCl + CuO +</td>
</tr>
<tr>
<td>(CuCl)LaNaNb₃O₁₀</td>
<td>Slope change at 772 °C</td>
<td>Na₀.₅La₀.₅Nb₂O₆ + “unidentified intermediate  LaNaNb₂O₇”</td>
</tr>
<tr>
<td></td>
<td>Exotherm 890 °C</td>
<td>Intermediate  \rightarrow  LaNbO₄ + NaNbO₃ + “Ca₂Nb₂O₇ and Ca₂Nb₂O₆ type structures”</td>
</tr>
</tbody>
</table>
KLaNaNb$_3$O$_{10}$ is the only compound of the series that does not show any sign of decomposition after heating to 1000 °C. As a result, the product can easily be obtained by direct reaction using the same experimental conditions used for the synthesis of RbLaNaNb$_3$O$_{10}$. The metastability of the other ion exchanged layered perovskites, decomposing before 800 °C, supports the need for the topotactic approach to these compounds as they cannot be obtained by traditional ceramic methods. LiLaNaNb$_3$O$_{10}$ undergoes a single step exothermic decomposition leading to the formation of LiNbO$_4$, NaNbO$_3$ and LaNbO$_3$. These compounds are common decomposition products for layered niobates as reported by Hermann and Wiley.$^{26}$ However, it is important to note the difference with LiCa$_2$Nb$_3$O$_{10}$, which with a two-step decomposition, leads to more complex decomposition products (CaNb$_2$O$_6$, Ca$_2$Nb$_2$O$_7$ and Li$_2$O).

HLaNaNb$_3$O$_{10}$ and NaLaNaNb$_3$O$_{10}$ both form hydrates, with the insertion of 1.2 and 2 moles of H$_2$O in the interlayer, respectively. HLaNaNb$_3$O$_{10}$ further undergoes the deintercalation of half a mole of H$_2$O to form a compound isostructural with Ca$_4$Nb$_6$O$_{19}$. Assuming La and Na still share the same atomic position, and based on the study by Fang et al,$^{23}$ a decomposition pathway is proposed with the first step being a condensation reaction:

$$2\text{HLaNaNb}_3\text{O}_{10} \rightarrow ^\cdot(\text{LaNa})_4\text{Nb}_6\text{O}_{19}^- + \text{H}_2\text{O} \quad (1)$$

The intermediate compound then dissociates as described by equation 2

$$^\cdot(\text{LaNa})_4\text{Nb}_6\text{O}_{19}^- \rightarrow \text{LaNbO}_4 + \text{NaNbO}_3 + 2^\cdot\text{Na}_{0.5}\text{La}_{0.5}\text{Nb}_2\text{O}_6^- \quad (2)$$
After dehydration, NaLaNaNb$_3$O$_{10}$ decomposed into NaNbO$_3$ and LaNbO$_4$ as final products. The broad decomposition temperature range, along with the absence of an exotherm highlights the resistance of this compound to decomposition. Several scientists have reported the presence of two phases for NaCa$_2$Nb$_3$O$_{10}$,\textsuperscript{11,12} low-temperature β- and irreversible high-temperature α-phases. Guertin et al.\textsuperscript{19} highlighted the fact that the latter one does not start decomposing until 800 °C and that the total decomposition does not readily occur, requiring extended heating periods at high temperatures.

(CuCl)LaNaNb$_3$O$_{10}$ exhibited the most complex decomposition process undergoing three distinct weight loss steps. An initial slope change was observed in the TGA plot at 600 °C, but the XRD pattern remained the same until the evident sharp weight loss at 650 °C. The initial loss of half a mole of Cl from the interlayer resulted in a rearrangement of the atoms to form Na$_{0.5}$La$_{0.5}$Nb$_2$O$_6$ along with CuO and CuCl according to the XRD data. At 830 °C, right before the final weight loss, both the final and the intermediate products are present in the sample. Further heating leads to the formation of LaNbO$_4$ and NaNbO$_3$ along with structures similar to that of Ca$_2$Nb$_2$O$_7$ and CaNb$_2$O$_6$. While Ca$_2$Nb$_2$O$_7$ was previously observed as a final product in the decomposition of (CuCl)Ca$_2$Nb$_3$O$_{10}$, CaNb$_2$O$_6$ was only found in the decomposed products of A’Ca$_2$Nb$_3$O$_{10}$ (A’= H, NH$_4$, Li) further highlighting the difference between the two series.

Josepha et al. reported the thermal behavior of neodymium-niobate layered perovskites,\textsuperscript{27} and discussed the fact that the size of the innerlayer A cation (Nd versus La) in the perovskite slab plays an important role in the stability of the compound. The niobates containing the smaller Nd cations decomposed at temperatures over 20 °C lower than the corresponding La compounds, attributing part of the lower thermal stability of the Nd compounds to structural distortion in the perovskite slab. Despite a more important out-of-plane distortion of the NbO$_6$ octahedra seen in
RbLaNaNb$_3$O$_{10}$ and the copper chloride compound with respect to that observed in the ACa$_2$Nb$_3$O$_{10}$ compounds, the bigger size of the A atoms might play an important role in the stability of the ALaNaNb$_3$O$_{10}$ series. Comparing results with that presented by Guertin et al.,$^{19}$ the mixed A-site alkali metal compounds in this chapter decompose at temperatures 30 °C higher than the calcium niobates further highlighting their stability due to the mixed A site.

### 3.5 Conclusions

The new solid-solution RbLaNaNb$_3$O$_{10}$ was successfully obtained at 1150 °C and shows a rare site sharing of trivalent and monovalent cations in the perovskite slab. This compound was proven to be highly receptive to topochemical manipulations, readily undergoing ion exchange reactions under 500°C to form the new series of triple layered perovskites A’LaNaNb$_3$O$_{10}$ (A’=H, Li, Na, K and CuCl). TGA-DSC studies examined the metastability of the ion-exchange products under 800 °C, with the exception of KLaNaNb$_3$O$_{10}$ that can also be obtained through direct reaction. While the H, Li and Na compounds decompose into simple perovskites, the copper chloride showed a more complex decomposition pathway to lead to new layered compounds. The results gave great insight into the temperature range accessible for the future topochemical manipulation of this new series of compounds.

### 3.6 References

Chapter 4

Synthesis and characterization of the triple-layered manganate perovskite RbLaCaNb$_2$MnO$_{10}$ and the ion exchange series, A’LaCaNb$_2$MnO$_{10}$ (A’= Li, K, Cs, CuCl)

4.1 Introduction

Layered perovskite such as Dion-Jacobson and Ruddlesden-Popper phases have been synthesized with a great variety of cations occupying the A and B sites of the perovskite slabs. While d$^0$ cations such as Nb$^{5+}$ in RbLaNb$_2$O$_7$, Ta$^{5+}$ in K$_2$SrTa$_2$O$_7$, and Ti$^{4+}$ in K$_2$La$_2$Ti$_3$O$_{10}$ are often favored for the B site, non-d$^0$ first row transition metals such as Fe, Cu and Mn have successfully been found in the B site of the perovskites. Layered manganates with the perovskite structure have triggered a lot of interest due to their appealing properties including giant and colossal magnetoresistance; Moritomo et al. reported the giant magnetoresistance of La$_{1-x}$Sr$_x$MnO$_3$ solid solution as an effect of the interaction of the Mn$^{3+}$ and Mn$^{4+}$ ions arising from the doping of the A site. Indeed, the particularity of manganese resides in its numerous possible oxidation states that can lead to very interesting magnetic and other physical properties. Mn can be found as the sole occupant of the B site as in La$_{1-x}$Sr$_x$MnO$_3$ and Ca$_4$Mn$_3$O$_{10}$ or be introduced into the perovskite slab along with d$^0$ transition as in the solid solutions Na$_2$Ln$_2$Ti$_3-x$Mn$_x$O$_{10}$ (Ln = Sm, Eu, Gd and Dy; 0 < x < 1) and Sr$_{2-x}$Ln$_{1+x}$Mn$_2$O$_7$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, and Er; 0 ≤ x ≤ 0.5).
In the work presented herein, the high temperature synthesis and thermal and magnetic behavior of the new DJ phase RbLaCaNb$_2$MnO$_{10}$, where Mn$^{4+}$ ions occupy the B site of the perovskite slab is described. The cesium analogue can also be obtained through ceramic methods. Ion exchange reactions with RbLaCaNb$_2$MnO$_{10}$ were explored and these produced the series A’LaCaNb$_2$MnO$_{10}$ (A’=Li, K and CuCl).

4.2 Experimental

4.2.1 Synthesis

ALaCaNb$_2$MnO$_{10}$ (A = Rb, Cs) were prepared by ceramic method from A$_2$CO$_3$ (A= Rb Alfa Aesar, 99%; Cs Alfa Aesar, 99.994%), La$_2$O$_3$ (Alfa Aesar, 99.99%), CaCO$_3$ (Alfa Aesar, 99.99%), Nb$_2$O$_5$ (Alfa Aesar, 99.9985%) and MnO$_2$ (Alfa Aesar, 99.997%). La$_2$O$_3$ and Nb$_2$O$_5$ were heated to 1000 °C for 24 h before reaction to remove any hydroxide or carbonate impurities. Stoichiometric amounts of the oxides along with 25% excess of A$_2$CO$_3$ were ground together and calcinated at 850 °C for 24 h in an alumina crucible, reground, and heated at 1150 °C for 24 h. Post reaction, the mixture was washed with hot distilled water to remove any unreacted material, rinsed with acetone using suction filtration, followed by a drying step at 100 °C for 12 h.

Ion exchange reactions were conducted to obtain the new A’LaCaNb$_2$MnO$_{10}$ compounds (A’= Li, K). RbLaCaNb$_2$MnO$_{10}$ was ground in a 1:10 molar ratio with LiNO$_3$ (Alfa Aesar, 99%) and KNO$_3$ (Alfa Aesar, 99.994%), and heated for 2 days at 350 °C and 7 days at 400 °C, respectively. (CuCl)LaNaNb$_3$O$_{10}$ was obtained through co-exchange reaction. RbLaCaNb$_2$MnO$_{10}$ and anhydrous CuCl$_2$ (Alfa Aesar, 99.995%) were mixed in a 1:2 molar ratio and finely ground together in an argon-filled glovebox using a mortar and pestle. The mixture
was pressed into pellets using a hand press (Sigma Aldrich), sealed under vacuum in a Pyrex tube, and heated at 350 °C for 3 days. The products were washed with copious amounts of hot water to remove unreacted starting material and rubidium by-products, rinsed with acetone, and dried overnight at 100 °C. Efforts were made to obtain the proton and sodium analogues; while preliminary results showed evidence for ion exchange based on the shift of the first reflection towards higher angles along with a change in the overall pattern, the resulting compounds were poorly crystalline.

4.2.2 Characterization

All compounds were characterized by X-ray powder diffraction (XRD) using a Philips X’Pert PW 3040 MPD system with a graphite monochromator (Cu Kα radiation, λ = 1.54056 Å). The regular scans were collected in the range of 3 – 75 °2θ in continuous mode. Data used for structure refinement were collected in the range of 5 – 110 °2θ. Lattice parameters were refined using JANA2006 program.

Crystal structure refinement for RbLaCaNb2MnO10 was performed using the Rietveld technique with the GSAS program. Refined parameters included scale factor, zero-point shift, background, cell constants, atomic positions and peak shape.

Stoichiometric compositions were examined by energy dispersive spectroscopy (EDS) on a JEOL JSM 5410 scanning electron microscope (SEM) equipped with an EDAX-DX Prime Microanalytical system. All ratios were normalized to niobium.

Magnetic measurements (ZFC/FC and hysteresis loops) were performed on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-7) in the temperature range of 4 K and 300 K in magnetic fields of 100 Oe.
Thermal analysis was carried out by thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) using a TA Instrument SDT Q600. Measurements were performed in alumina pans under flowing Ar and H₂-Ar from room temperature to 1000 °C at a heating rate of 10 °C/min.

4.3 Results

4.3.1 Synthesis and Structure

RbLaCaNb₂MnO₁₀ was obtained following the same steps as previously described for the synthesis of RbLaNaNb₃O₁₀ (Chapter 3), leading to another compound isostructural to RbCa₂Nb₃O₁₀₁¹ as shown in Figure 4.1.

![Figure 4.1](image)

Figure 4.1 Powder X-ray diffraction patterns for (a) RbCa₂Nb₃O₁₀, (b) RbLaNaNb₃O₁₀ and (c) RbLaCaNb₂MnO₁₀.
In a similar manner as the RbLaNaNb$_3$O$_{10}$, heating at very high temperatures was required to prevent the formation of the double layered phase RbLaNb$_2$O$_7$. Elemental analysis with EDS gave the following composition 0.80(6):1.3(3):1.2(2):2:1.0(2) for the Rb:La:Ca:Nb:Mn ratio, this being close to the expected ratio of 1:1:1:2:1. Table 4.1 shows the refined unit cell parameters for RbLaCaNb$_2$MnO$_{10}$ and RbCa$_2$Nb$_3$O$_{10}$. The two cells are comparable in size.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbLaCaNb$<em>2$MnO$</em>{10}$</td>
<td>3.8754(1)</td>
<td>14.9443(6)</td>
</tr>
<tr>
<td>RbCa$_2$Nb$<em>3$O$</em>{10}$</td>
<td>3.85865(6)</td>
<td>14.9108(3)</td>
</tr>
</tbody>
</table>

Structural refinement of RbLaCaNb$_2$MnO$_{10}$ was attempted using the Rietveld method. The starting model was based on RbCa$_2$Nb$_3$O$_{10}$ where the atomic positions were kept the same but La and Ca were constrained to the same position, both with 50 % occupancy. Based on previous reports on the ordering of the B-site,$^{12,13}$ the structural refinement began with Mn occupying the central position in the perovskite slab and Nb in the outside layers, both at 100 % occupancy in their respective sites. While the model produced reasonable agreement factors and presented a good fit of the pattern, the thermal parameters of the manganese became negative while that of the central oxygen atom was unreasonably large, along with the $\chi^2$. When Mn and Nb were allowed to share the two sites randomly, the refinement showed a preference for the manganese atoms to be in the center of the perovskite slabs as expected, but approximatively 10 % of the outside layers where occupied by the Mn. This random sharing of the B sites by the two cations, however, resulted in a large increase in all the oxygen thermal parameters. It was then concluded that the original model with Mn in the center of the perovskite slabs was preferred,
but with the thermal parameters fixed at 0.025 for the rest of the refinement. The observed, calculated and difference plots are shown in Figure 4.2, and the structural data with bond distances in Tables 4.2 and 4.3, respectively. The proposed structure can be seen in Figure 4.3.

![Graph showing intensity vs position, 20](image)

**Figure 4.2** Calculated (solid line), experimental (crosses) and difference (lower line) plots for the Rietveld refinement of RbLaCaNb$_2$MnO$_{10}$.

**Table 4.2** Crystallographic data for RbLaCaNb$_2$MnO$_{10}$.\(^a\)

<table>
<thead>
<tr>
<th>atom</th>
<th>g(^b)</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>1.0</td>
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<td>0.5</td>
<td>0.5</td>
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<tr>
<td>La/Ca</td>
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<td>0.5</td>
<td>0.5</td>
<td>0.1341(2)</td>
</tr>
<tr>
<td>Mn</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nb</td>
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<td>0.2843(2)</td>
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<tr>
<td>O1</td>
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<td>0</td>
<td>0.5</td>
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</tr>
<tr>
<td>O2</td>
<td>1.0</td>
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<td>0</td>
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<tr>
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<td>1.0</td>
<td>0</td>
<td>0.5</td>
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</tr>
<tr>
<td>O4</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0.416(1)</td>
</tr>
</tbody>
</table>

P4/mmm, Rp = 14.11%, wRp = 18.94%, $\chi^2 = 6.138$; \(^a\)U\(_{iso}\) were all constrained to 0.025; \(^b\)occupancy
Table 4.3 Selected bond distances for RbLaCaNb$_2$MnO$_{10}$

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
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<tbody>
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<td>Rb-O4 (x8)</td>
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<tr>
<td>La/Ca-O1 (x4)</td>
<td>2.789(2)</td>
</tr>
<tr>
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<td>2.749(1)</td>
</tr>
<tr>
<td>La/Ca-O3 (x4)</td>
<td>2.666(8)</td>
</tr>
<tr>
<td>Mn-O1 (x4)</td>
<td>1.93771(6)</td>
</tr>
<tr>
<td>Mn-O2 (x2)</td>
<td>1.78(1)</td>
</tr>
<tr>
<td>Nb-O2 (x1)</td>
<td>2.46(1)</td>
</tr>
<tr>
<td>Nb-O3 (x4)</td>
<td>1.981(2)</td>
</tr>
<tr>
<td>Nb-O4 (x1)</td>
<td>1.97(2)</td>
</tr>
</tbody>
</table>

Figure 4.3 Proposed structure of RbLaCaNb$_2$MnO$_{10}$. 
4.3.2 Magnetic Behavior

Magnetic measurements were performed on RbLaCaNb$_2$MnO$_{10}$ in a field of 100 Oe. The ZFC and FC curves, shown in Figure 4.4 along with the hysteresis loop at 2K, split at 275 °C indicating that RbLaCaNb$_2$MnO$_{10}$ is magnetically ordered over most of the studied temperature range. The magnetic moment was calculated from the linear fit at high temperature ranging between 3.3 and 4.9 depending on the sample. This value varies relative to the expected value of 3.87 for Mn$^{4+}$ ions. It is possible that not all the manganese ions are present in the +4 oxidation state leading to a variation in the overall magnetic moment. A sharp low temperature transition is observed at 43 K in both ZFC and FC curves. The hysteresis loops collected at 2, 23 and 43 K all show evidence for ferromagnetic behavior of the compound at those temperatures. The ferromagnetic behavior prevails at low temperatures and remains present up to ~ 150 K. The calculated Weiss constant of 237 K further supports the idea of ferromagnetic interactions in the compound.

![Figure 4.4](image)

Figure 4.4 (a) Magnetic susceptibility as a function of the temperature and (b) Hysteresis loop at 2 K for RbLaCaNb$_2$MnO$_{10}$. 

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4.3.3 Thermal Behavior

Thermogravimetric analysis and differential scanning calorimetry were conducted on RbLaCaNb$_2$MnO$_{10}$ in both oxidizing and reducing atmospheres. The DSC data show no distinct thermal events in either atmosphere. The compounds appear to be stable in oxidizing atmosphere until the end of the measurement at 1000 °C. An initial weight loss below 200 °C was attributed to the loss of surface water. A slight weight gain (≥ 0.1 wt%) after 300 °C was observed in some of the runs, but was not reproducible from sample to sample. The XRD pattern of the resulting compound is identical to the initial compound. Under reducing atmosphere, the material undergoes two consecutive weight losses with the first one of 0.8 wt% at 720 °C and the second one initiating at 880 °C without reaching a plateau before the end of the measurement at 1000 °C. The sample, originally black, turned dark brown in color. The XRD pattern after TGA was basically unchanged, however with the presence of two additional reflections at 32 and 46 °2θ. After reaction in reducing atmosphere, the same sample was heated under oxidizing atmosphere up to 1000 °C the sample turned back to its original black color. The TGA data (Figure 4.5) shows a weight loss from room temperature to 400 °C immediately followed by a small weight gain reaching a plateau at 700 °C. The resulting XRD pattern shows that the previously observed extra reflections disappeared, returning to the original RbLaCaNb$_2$MnO$_{10}$ pattern.
Figure 4.5 TGA curves for RbLaCaNb$_2$MnO$_{10}$ under (a) H$_2$-Ar and (b) additional heating under O$_2$-Ar.

4.3.4 Ion Exchange Products

The rubidium cation in the interlayer can be easily exchanged for other alkali metals to form A’LaCaNb$_2$MnO$_{10}$ (A’= Li and K). It can also undergo co-exchange to obtain the copper chloride compound, (CuCl)LaCaNb$_2$MnO$_{10}$. Elemental analysis confirmed the success of the ion exchange reactions as minimal amounts of rubidium (< 5%) were retained in the sample. Figure 4.6 shows a comparison of the XRD data collected for the different ion exchange products as well as the cesium analogue obtained through direct reaction. The new series is isostructural with the respective A’Ca$_2$Nb$_3$O$_{10}$ and A’LaNaNb$_3$O$_{10}$ series. All the compounds were indexed in the tetragonal system and the unit cell parameters are presented in Table 4.4.
Table 4.4 Refined unit cell parameters for the ALaCaNb₂MnO₁₀ series.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
<th>Layer spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiLaCaNb₂MnO₁₀</td>
<td>7.729(1)</td>
<td>28.559(7)</td>
<td>1706.04</td>
<td>14.28</td>
</tr>
<tr>
<td>KLaCaNb₂MnO₁₀</td>
<td>7.705(2)</td>
<td>14.691(3)</td>
<td>872.16</td>
<td>14.69</td>
</tr>
<tr>
<td>RbLaCaNb₂MnO₁₀</td>
<td>3.87532(9)</td>
<td>14.9447(5)</td>
<td>224.44</td>
<td>14.94</td>
</tr>
<tr>
<td>CsLaCaNb₂MnO₁₀</td>
<td>3.8802(3)</td>
<td>15.094(2)</td>
<td>227.25</td>
<td>15.09</td>
</tr>
<tr>
<td>(CuCl)LaCaNb₂MnO₁₀</td>
<td>3.8611(1)</td>
<td>15.651(2)</td>
<td>233.33</td>
<td>15.61</td>
</tr>
</tbody>
</table>

Figure 4.6 XRD patterns of the ALaCaNb₂MnO₁₀ series with (a) Li, (b) K, (c) Rb, (d) Cs and (e) CuCl.
4.4 Discussion

A new layered manganate RbLaCaNb$_2$MnO$_{10}$ was synthesized through a high temperature method by substitution of both A and B sites of the triple layered RbCa$_2$Nb$_3$O$_{10}$,\textsuperscript{11} resulting in an isostructural compound (Figure 1). The unit cell parameters of the new compound are comparable to those of RbCa$_2$Nb$_3$O$_{10}$ (Table 1) with a slightly larger $c$ parameter despite the smaller size of the Mn in the B site. In order to solve the structure, it was important to determine the distribution of the elements in the different sites. La and Ca were randomly distributed in the A site while an ordering of the B site was observed; the latter is expected based on the other previously reported compounds.\textsuperscript{12,13} While reporting the structure of the Aurivillius phase Bi$_2$Sr$_2$Nb$_2$MnO$_{12-\delta}$, Yu et al. discussed the ordering of the B site in a Nb$^{5+}$–Mn$^{4+}$–Nb$^{5+}$ sequence.\textsuperscript{12} It appears that ions with unpaired d electrons tend to favor the middle layer of the perovskite slab. This is related to the second-order Jahn-Teller distortion in the outer layers of various Dion-Jacobson layered perovskites, which requires a $d^0$ electron configuration;\textsuperscript{14} non-$d^0$ are not stable in these sites and tend to favor the inner B-sites. Similar observations were made throughout the refinement of RbLaCaNb$_2$MnO$_{10}$ as a random distribution of the cations in the two B sites was attempted but only a minimum amount of Mn would be found in the outer layers.

In both RbLaCaNb$_2$MnO$_{10}$ and RbCa$_2$Nb$_3$O$_{10}$ the perovskite slab consists of a small, contracted inner octahedron surrounded by two highly distorted ones. When looking at the bond lengths of the central octahedron, the equatorial Mn–O1 is 1.93771 Å which is comparable to that of other manganese oxides such as Ca$_4$Mn$_3$O$_{10}$\textsuperscript{7} (1.897 Å) and almost the same as that of the corresponding Nb–O1 bond length in RbCa$_2$Nb$_3$O$_{10}$ (1.92932 Å). The main difference is in the apical Mn–O2 bond which is significantly shorter at 1.78 Å vs 1.877, consistent with the smaller
size of the Mn\textsuperscript{4+} (0.67 Å) in comparison with Nb\textsuperscript{5+} (0.78 Å) in the same octahedral coordination.\textsuperscript{15} The contraction of the bond is similar too, but not as drastic as the one observed in Bi\textsubscript{2}Sr\textsubscript{2}Nb\textsubscript{3}MnO\textsubscript{12-δ}.\textsuperscript{12} Along with this contraction comes the simultaneous elongation in the opposite direction of the Nb–O2 bond at 2.46Å (vs 2.379 in RbCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}), towards the interlayer. The Nb atoms sit in distorted octahedra, which is consistent with the fact that d\textsuperscript{0} cations favor asymmetric coordination in such Dion-Jacobson layered perovskites.

Despite the results of the elemental analysis it is possible that we do not actually meet the exact 2 to 1 Nb to Mn ratio but instead a more general Nb\textsubscript{3-x}Mn\textsubscript{x} composition as seen in most solid solutions based on the substitution of the B site by Mn. Schaak et al. discussed the difficulty to obtain a pure x = 1 phase when the A site is occupied by a large La\textsuperscript{3+} compared to smaller lanthanides as in Na\textsubscript{2}A\textsubscript{2}Ti\textsubscript{3-x}Mn\textsubscript{x}O\textsubscript{10}.\textsuperscript{8} Additionally, due to the different oxidation states seen for manganese it is most likely that some Mn\textsuperscript{3+} is present in the sample and would create oxygen vacancies. Yu et al. reported the vacancy being in the equatorial O1 position.\textsuperscript{12} This could explain why a big thermal parameter was observed in the early stage of the refinement before the parameters were fixed.

Efforts to confirm the oxidation state by thermal analysis under oxidative and reductive atmospheres were carried out. It was assumed that all the Mn\textsuperscript{4+} present in the perovskite layer would get reduced to Mn\textsuperscript{3+} and Mn\textsuperscript{2+} consecutively upon heating. The first weight loss observed under H\textsubscript{2}-Ar (Figure 5) was smaller than expected if all Mn were present in the 4+ state (exp: 0.85 wt% vs calc: 1.20 wt%). On the other hand, a small weight gain was observed under O\textsubscript{2} at 400 °C which might be related to some Mn\textsuperscript{3+} being oxidized to Mn\textsuperscript{4+}. It appears that heating under O\textsubscript{2} leads to an even more crystalline sample as the peaks observed on the XRD pattern were more defined and more intense compared to that before the TGA analysis. The change in
oxidation state to +3 or +2 under H\_2 does not appear to put a strain on the structure in that the compound resists decomposition to simpler compound(s) under these conditions. However, the presence of new reflections led us to think that the compound undergoes a slight modification, possibly accommodating oxygen vacancies in the structure. Interestingly, this phase transition appears to be reversible when followed by heating under O\_2. The color change of the sample going from black to dark brown and back to black is another indication of a possibly reversible reaction.

RbLaCaNb\_2MnO\textsubscript{10} has interesting magnetic behavior. The ZFC and FC curves split early on at approximately 270-275 K as a sign of magnetic irreversibility. One magnetic transition occurs at 43 K in both the ZFC and FC curves with the formation of an ordered state below this temperature. It is not unusual for manganese oxides to undergo magnetic transitions at low temperatures. It is possible that this transition is associated with a structural transition as well. The magnetic moment calculated from the linear fit of the reciprocal susceptibility varies with the sample, sometimes close to that of Mn\textsuperscript{3+} and other times much lower in contrast with the expected moment of 3.87\muB for Mn\textsuperscript{4+}. As mentioned previously, this would support the idea that the manganese ions are not exclusively present in the +4 oxidation state; other oxidation states can be present in the compound, most likely Mn\textsuperscript{3+}, which would have an effect on the magnetic behavior and the moment.

Ion exchange can readily be conducted to synthesize different analogues of the series. Compounds such as A’LaCaNb\_2MnO\textsubscript{10} (A’= Li and K) can be prepared in a similar manner as seen in the A’Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} series.\textsuperscript{16} Furthermore, it is expected that exchange of the rubidium for a proton and sodium should be possible. For comparison, the cesium analogue was successfully obtained through ceramic method. An increase in layer spacing and volume (Table 4) is observed
going from Li to Cs following the expected ionic size trends.\textsuperscript{15} Reaction with CuCl\(_2\) to form (CuCl)LaCaNb\(_2\)MnO\(_{10}\) led to an increase of 0.7 Å in c parameter with respect to the Rb phase, which is in agreement with previous results reporting the construction of metal halides in the interlayer.\textsuperscript{16,17}

### 4.5 Conclusions

The new Dion-Jacobson phase RbLaCaNb\(_2\)MnO\(_{10}\) was synthesized through ceramic method. The compound exhibits an ordering of the B site in the perovskite slab with the manganese sitting in the center of the layer. Magnetic measurements showed a clear magnetic transition at 43 K, present in both ZFC and FC curves. Ferromagnetic behavior is observed at low temperatures up to at least 150 K. Thermal studies under both reductive and oxidative atmospheres showed the stability of the structure at high temperature throughout the change in oxidation state of the manganese ions. RbLaCaNb\(_2\)MnO\(_{10}\) was proven to be receptive to ion exchange reaction with nitrates to readily form the Li and K analogues or CuCl\(_2\) to obtain the new copper chloride compound (CuCl)LaCaNb\(_2\)MnO\(_{10}\).

### 4.6 References

Chapter 5

Synthesis and characterization of new double layered perovskites MSrTa$_2$O$_7$ (M= Co and Zn) obtained through ion exchange of K$_2$SrTa$_2$O$_7$

5.1 Introduction

Research on Ruddlesden-Popper (RP) compounds, with general formula A$_2'$[A$_{n-1}$B$_n$O$_{3n-1}$] where A=alkali metal, A'=rare earth or alkaline-earth, B=transition metal, n=number of perovskite layers, show a predisposition to be topochemically modified at low temperatures through a wide variety of reactions. Like in the Dion Jacobson (DJ) phases, the interlayer alkali cations can be easily replaced by smaller monovalent cations such as H$^+$, Li$^+$ or even Ag$^+$ using the same molten salt approach. Aqueous ion exchange has also proven to be effective to go the opposite way, as described by Schaak and Mallouk to obtain KLnTiO$_4$ (Ln, La, Nd, Sm, Eu, Gd, Dy) from HLnTiO$_4$ by reaction with KOH. Inorganic-organic RP hybrids were reported after the intercalation and grafting of organic substituents in the interlayer which could potentially lead to interesting properties. Ion exchange reactions on several RP phases allowed for the connection between the different families of layered perovskites. Gopalakrishnan et al. were able to convert triple layered K$_2$La$_2$Ti$_3$O$_{10}$ into the corresponding Aurivillius phase by reaction with BiOCl while aliovalent ion exchange of alkali metal for divalent alkaline earth metals chlorides such as SrCl$_2$ created a bridge between the RP and DJ phases. The exchange of two monovalent interlayer cations for one divalent cation such as Ca$^{2+}$ creates vacancies in the interlayer potentially opening for further topochemical manipulations. Based on this idea,
McIntyre et al. used a multistep approach to synthesize the mixed-valence titanate Na$_{x+y}Ca_{x/2}LaTiO_4$ from RP NaLaTiO$_4$ by ion exchange reaction with Ca(NO$_3$)$_2$ followed by reductive intercalation with sodium metal vapors.$^{10}$ Ion exchange reaction with first row d$^n$ (n≠0) transition metals has been investigated through aqueous and molten salt reactions. Triple layered M$^{III}$Eu$_2$Ti$_3$O$_{10}$ (M=Co, Cu and Zn) and Li$_{0.3}$Ni$_{0.85}$La$_2$Ti$_3$O$_{10}$ were obtained by reaction at low temperatures of the RP compounds with corresponding nitrate and chloride solutions, respectively.$^{11,12}$ Kim et al. and Hyeon et al. reported the synthesis of single and triple layered lanthanum titanates, respectively, containing Co, Cu or Zn in the interlayer through molten salt reaction with MCl$_2$-KCl molten mixture.$^{13,14}$ We extended the series with the iron analogue presented in Chapter 2 obtained by direct ion exchange. While several examples of ion exchange reactions involving single or triple layered RP perovskites are present in the literature, no report of such reactions with double layered RP perovskites was found. Herein, we present the synthesis of new double layered MSrTa$_2$O$_7$ compounds where M is a non-d$^0$ transition metal obtained through topochemical synthesis.

5.2 Experimental

5.2.1 Synthesis

$K_2SrTa_2O_7$ – $K_2SrTa_2O_7$ was synthesized as reported in the literature.$^{15}$ Stoichiometric amounts of KOH (Alfa Aesar, 99.98%), SrCO$_3$ (Alfa Aesar, 99.99%) and Ta$_2$O$_5$ (Alfa Aesar, 99%) were ground together and the mixture was heated in an alumina crucible in a box furnace at 850 °C for 24 h and 1050 °C for an additional 24 h one intermediate grinding. After reaction the white product was washed with large amounts of hot DI-water, rinsed with acetone in a Büchner funnel, and then dried for 12 hours at 110 °C. Phase purity was verified by X-ray
powder diffraction (XRD). Since the compound readily forms a hydrate, $K_2\text{SrTa}_2\text{O}_7\cdot2\text{H}_2\text{O}$, the sample was placed in an argon-filled glovebox directly after reaction. The powder pattern was refined on a tetragonal unit cell with $a = 3.9466(3)$ Å and $c = 21.5701(5)$ Å, in agreement with the literature.\(^{15}\)

$MSr\text{Ta}_2\text{O}_7$ - $MSr\text{Ta}_2\text{O}_7$ products with $M = \text{Co}$ and $\text{Zn}$ were synthesized through ion exchange. $K_2\text{SrTa}_2\text{O}_7$ and $\text{MCl}_2$ ($M = \text{Co Alfa Aesar, 99.7% and Zn Alfa Aesar, 99.999%}$), were ground together at a 1:2 molar ratio in an argon-filled glove box and pressed into pellets using a hand press. The pellets were heated under vacuum ($<10^{-4}$ Torr) in Pyrex tubes in a tube furnace. $\text{CoSrTa}_2\text{O}_7$ was obtained at 375 °C in 1 week and $\text{ZnSrTa}_2\text{O}_7$ was obtained at 350 °C in 2 weeks. After reaction, the blue (Co) and white (Zn) samples were washed with hot DI-water in order to remove any excess transition metal chloride and by-products, rinsed with acetone in a Büchner funnel, and dried overnight at 110 °C. Reactions to obtain other $MSr\text{Ta}_2\text{O}_7$ analogues with $M = \text{Fe, Ni, Cu, Mn}$ were carried out for 1 to 2 weeks at different temperatures (250 to 375 °C) but resulted in poorly crystalline compounds.

5.2.2 Characterization

All compounds were characterized by X-ray powder diffraction (XRD) using a Philips X’Pert PW 3040 MPD system with a graphite monochromator ($\text{Cu K}\alpha$ radiation, $\lambda = 1.54056$Å). The regular scans were collected in the range $3 – 75^\circ$ 2θ in a continuous mode. The data used for structure refinement were collected in the range $5 – 110^\circ$ 2θ. The lattice parameters were refined using JANA2006.\(^{16}\) Structure refinement was attempted using GSAS.\(^{17}\)

Stoichiometric compositions were examined by energy dispersive spectroscopy (EDS) on a JEOL JSM 5410 scanning electron microscope (SEM) equipped with an EDAX-DX Prime
microanalytical system. All ratios were normalized to tantalum. Only traces of potassium and chlorine were found in the samples.

Thermal analysis was carried out by thermogravimetric/differential thermal analysis (TGA/DTA) using a TA Instruments Thermal Analyst-2000. Measurements were performed in inert, oxidizing and reductive atmospheres between room temperature and 800 °C by heating samples at 10 °C/min in Ar and O\textsubscript{2}/Ar, respectively.

5.3 Results and Discussion

5.3.1 Synthesis and Structure

MSrTa\textsubscript{2}O\textsubscript{7} compounds (M = Co and Zn) were successfully obtained through aliovalent ion exchange reactions with the double layered Ruddlesden-Popper perovskite, K\textsubscript{2}SrTa\textsubscript{2}O\textsubscript{7}. Minor amounts of residual potassium were found in the samples (less than 5%) by EDS. Figure 5.1 shows the XRD patterns of the two transition metal compounds in comparison with the parent. The two new layered perovskites are isostructural with each other. The low angle reflection at 4.5 °2θ varied in intensity from sample to sample but was observed for both series of compounds. The patterns were originally indexed in a tetragonal unit cell with space group I4/mmm, but some minor reflections as well as the low angle one were not indexed. A primitive tetragonal unit cell was then used to index all the peaks and refine the unit cell parameters shown in Table 5.1. A contraction of the unit cell along the z axis is observed with a decrease of about 2 Å in the c parameter, which is consistent with the exchange of two K\textsuperscript{+} for the smaller Cu\textsuperscript{2+} and Zn\textsuperscript{2+}. As mentioned by Hyeon and Byeon in the case of the triple layered M\textsuperscript{II}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} (M= Co, Cu, Zn)\textsuperscript{14} the c-axis doubling indicates that the staggered conformation of the parent compound is most likely retained in the new structure. Figure 5.2 shows the XRD pattern of MSrTa\textsubscript{2}O\textsubscript{7}
compounds compared to the calculated pattern of the tetragonal model. A proposed structure is presented in Figure 5.3.

**Table 5.1** Refined unit cell parameters of K$_2$SrTa$_2$O$_7$ and MSrTa$_2$O$_7$ (M=Co, Zn)

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$SrTa$_2$O$_7$</td>
<td>3.9768(1)</td>
<td>21.7062(6)</td>
<td>344.99</td>
</tr>
<tr>
<td>CoSrTa$_2$O$_7$</td>
<td>3.9275(1)</td>
<td>19.586(1)</td>
<td>302.12</td>
</tr>
<tr>
<td>ZnSrTa$_2$O$_7$</td>
<td>3.9287(2)</td>
<td>19.715(1)</td>
<td>304.87</td>
</tr>
</tbody>
</table>

**Figure 5.1** X-ray diffraction patterns of (a) K$_2$SrTa$_2$O$_7$, (b) CoSrTa$_2$O$_7$ and (c) ZnSrTa$_2$O$_7$
Figure 5.2 XRD pattern of the isostructural compounds (a) CoSrTa$_2$O$_7$, (b) ZnSrTa$_2$O$_7$ compared to the (c) simulated model pattern

Figure 5.3 Model structure of MSrTa$_2$O$_7$
Cobalt and zinc cations are expected to be present in the tetrahedral sites in the interlayer forming edge-sharing MO₄ tetrahedral layer as in the M^{II}_{0.5}LaTiO₄ and M^{II}La₂Ti₃O₁₀ series (M= Co, Cu, Zn). In depth Rietveld refinement is needed to pinpoint the exact structure of the new double layered compounds. The filling of only half of the octahedral could be very interesting to explore further topochemical manipulations such as reductive intercalation with alkali metals in order to build new frameworks in the interlayer.

5.3.2 Thermal behavior

The thermal behavior of CoSrTa₂O₇ was studied by TGA-DSC under inert and oxidative atmospheres up to 800 °C. The TGA curves are presented in Figure 5.4 and the XRD patterns of the resulting products are shown in Figure 5.5.

Figure 5.4 TGA curves for CoSrTa₂O₇ in (a) Ar and (b) O₂-Ar (DSC signal in green, Exo is up)
Only one important weight loss of 3.7 - 4 wt% at 350 °C is observed when heating under argon (Figure 5.4a): no DSC thermal event is associated with this weight loss. The resulting XRD pattern (Figure 5.5b) shows that CoSrTa$_2$O$_7$ is still present after the experiment along with SrTa$_2$O$_6$ (JCPDS File No. 51-1683) and possibly some Co$_3$O$_4$ (JCPDS File No. 42-1467). Unlike what is seen with the triple layered compounds MLa$_2$Ti$_3$O$_{10}$ (M=Fe, Co, Cu, Zn), no evidence of cell contraction for CoSrTa$_2$O$_7$ was observed in this case. It is still unclear what thermal event the weight loss is related to.
TGA data collected under O\textsubscript{2} show several successive weight losses, two of them being associated with small exotherms at 253 and 359 °C as can be seen in Figure 4b. Additionally, further heating led to a weight gain starting at 755 °C associated with a slope change in the DSC signal. The XRD pattern of the resulting product (Figure 5.5c) shows here also the presence of CoSrTa\textsubscript{2}O\textsubscript{7} and the decomposition product SrTa\textsubscript{2}O\textsubscript{6}. SrTa\textsubscript{2}O\textsubscript{6} appears to be a favored decomposition product for the double layered strontium tantalates as H\textsubscript{2}SrTa\textsubscript{2}O\textsubscript{7} was already proven to dehydrate above 350°C to form this defective perovskite.\textsuperscript{18,19} More characterization, including high temperature XRD, is necessary to follow the decomposition of CoSrTa\textsubscript{2}O\textsubscript{7} as a function of the temperature.

Further reactions were attempted with other first row transition metals in order to expand the new series of double layered MSrTa\textsubscript{2}O\textsubscript{7} with M = Mn, Fe, Ni and Cu. Evidence is seen for the ion exchange as the pattern showed similar reflections to CoSrTa\textsubscript{2}O\textsubscript{7}. However, the poor crystallinity of the samples, despite trying long reaction times with MCl\textsubscript{2} and different temperatures, prevented any additional characterization. Reactions involving other transition metal halides such as bromides might prove more effective, possibly leading to more crystalline compounds.

5.4 Conclusions

New double layered perovskites MSrTa\textsubscript{2}O\textsubscript{7}, where M = Co and Zn were synthesized through ion exchange reactions at low temperatures (< 500 °C) with Ruddlesden-Popper phase, K\textsubscript{2}SrTa\textsubscript{2}O\textsubscript{7}. Initial structural refinement confirms the retention of the layered structure with the filling of half the tetrahedral sites in the interlayer by the transition metals. The two compounds were proven to be metastable undergoing decomposition to form the disordered perovskite
SrTa$_2$O$_6$. Additional work is needed to expand the new series of compounds to other transition metals and these structures might be receptive to further topochemistry such as intercalation.

5.5 References

Chapter 6

Concluding Remarks

The topic of the present dissertation is the synthesis of new layered perovskites focusing on two main areas of topochemistry: ion exchange and substitution reactions. Particular attention was given to the involvement of transition metals in the structure, either in the interlayer or the perovskite slab, due to the promise of new interesting properties that were also investigated.

Ion exchange reactions were used to bridge two of the main families of layered perovskites. We described the aliovalent ion exchange of the Ruddlesden-Popper triple layered Li$_2$La$_2$Ti$_3$O$_{10}$ with FeCl$_2$ to form the new Dion-Jacobson phase FeLa$_2$Ti$_3$O$_{10}$. The compound exhibit a spin glass transition below 30 K. One of the most interesting feature of the new iron phase is the significant cell contraction ($\Delta c \approx 2.7$ Å) occurring at higher temperatures, associated with a change in the oxidation state of iron (Fe$^{2+}$ to Fe$^{3+}$) and deintercalation of iron as Fe$_2$O$_3$ to produce Fe$_{0.67}$La$_2$Ti$_3$O$_{10}$. This was the first time that such behavior is observed for a product of topochemical manipulation since they often decompose into simpler, more thermodynamically stable structures. Structural analysis and Mössbauer studies were essential in the characterization of the new phase indicating that the local iron environment goes from tetrahedral to a distorted octahedral coordination upon oxidation of the iron.

Bridging the two families of perovskites using aliovalent ion exchange reactions open the door for more topochemical manipulations as two monovalent cations are replaced by a singular divalent cation, leading to the formation of vacancies in the interlayer that could eventually be filled using intercalation techniques. In order to offer a variety of starting materials we started
investigating the synthesis of new double layered perovskites carrying similar ion exchange reaction on K$_2$SrTa$_2$O$_7$ to form MSrTa$_2$O$_7$ with M= Co and Zn.

Using a different approach, two new triple layered DJ compounds were obtained by substitution of the A or B site and ion exchange reactions were successfully carried out on them illustrating the numerous compositional and structural variations that layered perovskites have to offer. RbLaNaNb$_3$O$_{10}$, with the unusual site sharing of La$^{3+}$ and Na$^+$, was successfully synthesized using ceramic method. Based on the idea of site sharing with cations of different oxidation states, the new manganate RbLaCaNb$_2$MnO$_{10}$ was also obtained by the “heat and beat” method and exhibits an ordering of the B site in the perovskite slab with the manganese sitting in the center of the layer, which is common for manganese oxides. Substitution of the B site with magnetic active manganese cation led to interesting magnetic behavior not observed in RbCa$_2$Nb$_3$O$_{10}$. The library of inorganic compounds was further expanded after the successful ion exchange of the interlayer species for new cationic species using different media (aqueous, molten, solid-state) leading to a new selection of starting materials for further topochemical manipulations.
Appendix A

Synthesis and ion exchange of new quadruple layered RbLaNa$_2$Nb$_4$O$_{13}$

A.1 Introduction

In 1985, Jacobson et al. reported the synthesis of multilayered perovskites K[Ca$_2$Na$_{3n}$Nb$_n$O$_{3n+1}$] (3 ≤ n ≤ 7) obtained via the solid-state reaction at high temperatures between the layered perovskite KCa$_2$Nb$_3$O$_{10}$ and the simple perovskite NaNbO$_3$.\(^1\) A few years later, this technique was also used to get RbCa$_2$NaNb$_4$O$_{13}$\(^2\) that later on was used as starting material for ion exchange reactions to form the copper-chloride (CuCl)Ca$_2$NaNb$_4$O$_{13}$ in an effort to get new magnetic materials.\(^3\) Using the 2-step approach and with the idea of continuing the work described in Chapter 3, the quadruple layered RbLaNa$_2$Nb$_4$O$_{13}$ was obtained by reacting stoichiometric amounts RbLaNb$_2$O$_7$ and NaNbO$_3$, with La and Na sharing the A site of the perovskite slab. Additionally, topotactic manipulations at low temperatures (< 500 °C) were attempted on the new products with ANO$_3$ (A = alkali metals) and copper chloride in order to expand the family of new layered perovskites. Details on the synthesis and characterization of this series of compounds are presented herein.
A.2 Experimental

- **Synthesis**

RbLaNb$_2$O$_7$ was obtained by a method similar to that previously reported by Gopalakrishnan et al.$^4$ Stoichiometric amounts of La$_2$O$_3$ and Nb$_2$O$_5$ were ground together with 25% excess of Rb$_2$CO$_3$. The mixture was heated at 850 °C for 12 h, reground, and heated for additional 24 h at 1050 °C. The sample was washed with hot distilled water and dried at 100 °C for 12 h. NaNbO$_3$ was synthesized by reaction of stoichiometric amounts of Na$_2$CO$_3$ and Nb$_2$O$_5$ at 800°C for 4 h then 900 °C for 5 h as found in the literature.$^5$ RbLaNa$_2$Nb$_4$O$_{13}$ was prepared by the solid state reaction of RbLaNb$_2$O$_7$ and NaNbO$_3$ in a 1:2 molar ratio for 2 days at 1250 °C with intermediate grindings. RbLaNaNb$_3$O$_{10}$ could also be prepared the same way from stoichiometric amounts of RbLaNb$_2$O$_7$ and NaNbO$_3$.

Initial ion exchange reactions were attempted on the new compounds using a 10-fold molar excess of LiNO$_3$ Alfa Aesar, 99.0 %) in order to form LiLaNa$_2$Nb$_4$O$_{13}$. The reactions were carried out in alumina combustion boat at 300-350 °C for 24 h. Similar reactions were attempted with sodium and potassium nitrates. Ion exchange reaction with CuCl$_2$ (Alfa Aesar, 99.995%) was also attempted following the method described by Kodenkandath et al.$^6$; a 1:2 molar ratio of starting material and CuCl$_2$ were reacted together under vacuum in a sealed Pyrex tube for several days at 350 °C. The sample was bright green at the end of the reaction with CuCl$_2$.

After being thoroughly washed with hot distilled water, the samples were dried overnight at 100 °C.
• **Characterization**

All materials were characterized using powder X-ray diffraction with a Philips X-pert PW 3040 MPD F-ray diffractometer with Cu Kα radiation. Data was collected over the range of 3°< \(2θ< 75°\). Lattice parameters were refined using Fullprof and Chekcell programs. Stoichiometric compositions were examined by energy dispersive spectroscopy (EDS) on a JEOL JSM 5410 scanning electron microscope (SEM) equipped with an EDAX-DX Prime microanalytical system.

### A.3 Results and Discussion

The synthesis of the quadruple layered compound was successful as shown by the diffraction data presented in Figure A.1.1. A shift of the first reflection towards lower angles is observed and confirms the cell expansion. The quadruple layered forms readily at high temperatures but heating at 1150 °C is not enough to get a pure phase. While no reflections are observed for remaining double layered RbLaNb₂O₇, the XRD pattern showed evidence for the triple layered phase RbLaNaNb₃O₁₀. Carrying the reaction at 1250 °C led a single phase material with no evidence for the presence of smaller perovskite structures.

A 1:1:2:3 Rb:La:Na:Nb atomic ratio was confirmed by elemental analysis. The unit cell parameters were refined based on a tetragonal unit cell and are presented in Table A.1. A continuous expansion along the c axis, observed going from RbLaNb₂O₇ to RbLaNaNb₃O₁₀ to RbLaNa₂Nb₄O₁₃, is consistent with the addition of NbO₆ octahedron in the perovskite slab. Similar behavior was observed by Jacobson et al. in the KCaNa\(_{n-3}\)Nb\(_n\)O\(_{3n+1}\) series.\(^1\) Figure A.2 shows the ideal structures for the different multiple layered compounds, from the simple perovskite NaNbO₃ to the quadruple layered RbLaNa₂Nb₄O₁₃.
Table A.1 Refined unit cell parameters of RbLaNa$_2$Nb$_4$O$_{13}$, RbLaNaNb$_3$O$_{10}$ and RbLaNb$_2$O$_7$

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbLaNa$_2$Nb$<em>4$O$</em>{13}$</td>
<td>3.893(6)</td>
<td>19.90(3)</td>
<td>287.85</td>
</tr>
<tr>
<td>RbLaNaNb$<em>3$O$</em>{10}$</td>
<td>3.886(2)</td>
<td>15.138(9)</td>
<td>228.62</td>
</tr>
<tr>
<td>RbLaNb$_2$O$_7$</td>
<td>3.885(2)</td>
<td>10.989(3)</td>
<td>165.86</td>
</tr>
</tbody>
</table>

Figure A.1 X-ray diffraction patterns of (a) RbLaNa$_2$Nb$_4$O$_{13}$, (b) RbLaNaNb$_3$O$_{10}$ and (c) RbLaNb$_2$O$_7$
Figure A.2 Idealized structures, from left to right, of NaNbO₃, RbLaNb₂O₇, RbLaNaNb₂O₁₀, and RbLaNa₂Nb₄O₁₃. The pink sphere represents the Rb atoms, the little green spheres represent La and Na atoms and the blue octahedral with the red spheres represent the NbO₆ units.

Ion exchange reactions were attempted on RbLaNa₂Nb₄O₁₃ using molten salts and copper chloride. The resulting patterns for the lithium and copper chloride samples are shown in Figure A.3. One can observe a change in pattern when compared to the parent compound as a sign of a modification of the structure of the compound as well as a shift of the first reflection to higher angles in the case of the lithium and to lower angle for the copper chloride, which is consistent with the exchange of Rb for Li and CuCl, respectively. XRD patterns of the products of the reactions with sodium and potassium nitrates show evidence for ion exchange reaction but the crystallinity of the compounds remained poor. The XRD pattern of the copper chloride sample is very similar to that of (CuCl)Ca₂NaNb₃O₁₀ reported by Kitada et al. A layer expansion of about 0.8 Å is observed for the copper chloride system which is in agreement with the 0.7 Å commonly observed for this kind of ion exchange on Dion-Jacobson layered perovskites.
A.4 Conclusions

A multistep approach was used for the synthesis of the $n = 4$ layered perovskite, RbLaNa$_2$Nb$_4$O$_{13}$ from RbLaNb$_2$O$_7$ and NaNbO$_3$ at high temperatures. The new layered compound has proven to be receptive to ion exchange with alkali metals and metal halides. This chemistry will allow us to expand the library of inorganic compounds and possibly lead to unusual properties.

A.5 References


Appendix B

Synthesis and characterization of new triple layered perovskite
$\text{Fe}_{0.5}\text{Cu}_{0.5}\text{La}_2\text{Ti}_3\text{O}_{10}$

B.1 Introduction

Ion exchange reactions have been extensively studied for both Dion-Jacobson and Ruddlesden-Popper layered perovskite series. Researchers, including our group, have been developing ion exchange techniques focusing on the interlayer cations involving an extensive selection of ions that can be used for the reactions. Alkali, alkaline earth and transition metals have all been proven to be good candidates for monovalent (e.g. $\text{ALaNb}_2\text{O}_7$ series with $\text{A}=\text{alkali metals}$) and aliovalent (e.g. $\text{M}_{0.5}\text{LaNb}_2\text{O}_7$ with $\text{M}=\text{Fe, Ni, Cu}$ and $\text{M}^{II}_{0.5}\text{LaTiO}_4$) ion exchanges or even co-exchange with metal halides (e.g. $(\text{CuCl})\text{LaTa}_2\text{O}_7$). Different media can be used to carry out those reactions, either aqueous or molten reactions and solid-state reaction with for example the use of hand-pressed pellets reacted under vacuum for an extended period of time. The common thing to most of the ion exchange reactions reported until now is the fact that only one type of cation (one element) is used at a time to replace the interlayer species.

Hyeon and Byeon reported the synthesis of new triple layered $\text{M}^{II}_{0.5}\text{La}_2\text{Ti}_3\text{O}_{10}$ with $\text{M}=\text{Co, Cu}$ and Zn using a molten-salt, eutectic mixture; and later on, Neiner et al. added the lithium analogue $\text{Li}_{0.3}\text{Ni}_{0.85}\text{La}_2\text{Ti}_3\text{O}_{10}$ to the series using aqueous solution of NiCl$_2$. We described in Chapter 2 that the iron analogue $\text{FeLa}_2\text{Ti}_3\text{O}_{10}$ can easily be obtained from $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ by pellet synthesis under vacuum at 350 °C for 5 days. We were also able to obtain the copper and zinc...
compounds by the same technique under the same condition. The work presented herein is the
extension of those ion exchange reaction with the challenge of exchanging the two lithium ions
for both iron and copper at the same time to obtain the mixed compound Fe_{0.5}Cu_{0.5}La_2Ti_3O_{10}.

B.2 Experimental

- **Synthesis**

  Starting material - Na_{2}La_{2}Ti_{3}O_{10} was synthesized as reported in the literature.\textsuperscript{12} Stoichiometric amounts of La_{2}O_{3} (Alfa Aesar, 99.99 %, dried at 1000 °C overnight to remove any hydroxides and carbonates) and TiO_{2} (Alfa Aesar, 99.9 %) were ground with a 20 % molar excess of Na_{2}CO_{3} (Alfa Aesar, 99.997 % anhydrous) to compensate for the loss of alkali metal oxide due to volatilization. The mixture was heated in an alumina crucible in a box furnace at 1050 °C for two days with two intermediate grindings. Li_{2}La_{2}Ti_{3}O_{10} was synthesized through an ion exchange reaction as seen in the literature.\textsuperscript{14} Na_{2}La_{2}Ti_{3}O_{10} and LiNO_{3} (Alfa Aesar, 99%, anhydrous) were mixed together in a 1:10 molar ratio and placed in a combustion boat in a tube furnace for 12 hours at 300 °C. For both Na_{2}La_{2}Ti_{3}O_{10} and Li_{2}La_{2}Ti_{3}O_{10}, after reaction the white products were washed with large amounts of DI-water, rinsed with acetone in a Büchner funnel, and then dried for 12 hours at 110 °C. Phase purity was verified for both starting materials by X-ray powder diffraction (XRD).

  Fe_{0.5}Cu_{0.5}La_{2}Ti_{3}O_{10} - Li_{2}La_{2}Ti_{3}O_{10}, FeCl_{2} (Alfa Aesar, 99.5% anhydrous) and CuCl_{2} (Alfa Aesar, 99.9%), were ground together at a 1:1:1 molar ratio in an argon-filled glove box and pressed into pellets using a hand press. The pellets were heated under vacuum (<10^{-4} Torr) in Pyrex tubes at 350 °C for 5 days. After reaction, the sample was washed with DI-water in order to remove any excess transition metal chloride and by-products, rinsed with acetone in a Büchner
funnel, and dried overnight at 110 °C. FeLa$_2$Ti$_3$O$_{10}$ and CuLa$_2$Ti$_3$O$_{10}$ were obtained by the same method using a 1:2 Li$_2$La$_2$Ti$_3$O$_{10}$:MCl$_2$ molar ratio

- **Characterization**

  All compounds were characterized by X-ray powder diffraction (XRD) using a Philips X’Pert PW 3040 MPD system with a graphite monochromator (Cu Kα radiation, λ = 1.54056Å) with the exception of the high-pressure samples that were analyzed using a Mo source. The regular scans were collected in the range 3 – 75° 2θ in a continuous mode. Lattice parameters were refined using Fullprof and Chekcell programs.

  Stoichiometric compositions were examined by energy dispersive spectroscopy (EDS) on a JEOL JSM 5410 scanning electron microscope (SEM) equipped with an EDAX-DX Prime microanalytical system. All ratios were normalized to titanium. Only traces of alkali metal and chlorine were found in the sample. The surface morphology was observed using a LEO 130 VP field emission scanning electron microscope (FESEM).

  Thermal analysis was carried out by thermogravimetric/differential thermal analysis (TGA/DTA) using a TA Instruments Thermal Analyst-2000. Measurements were performed in reducing and inert atmospheres between room temperature and 800 to 1000 °C by heating samples at 10 °C/min in H$_2$/Ar and Ar, respectively.

  Magnetic measurements (ZFC/FC and hysteresis loops) were performed on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-7) in the temperature range of 4 K and 300 K in magnetic fields of 100 Oe.
B.3 Results and discussion

- **Synthesis and structure**

**Target reaction**

\[
\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} + \frac{1}{2}\text{FeCl}_2 + \frac{1}{2}\text{CuCl}_2 \rightarrow \text{Fe}_{0.5}\text{Cu}_{0.5}\text{La}_2\text{Ti}_3\text{O}_{10} + 2\text{LiCl}
\]

The ion exchange reaction was carried out to replace the Li\(^+\) ions by both Fe\(^{2+}\) and Cu\(^{2+}\) at the same time. The elemental analysis of the final product indicated the ratio Fe:Cu:La:Ti 0.53(5):0.47(5):2.03(6):3; it is in really good agreement to the expected ratio of 0.5:0.5:2:3. The powder pattern for the resulting compound is presented in Figure B.1 in comparison with that of the two MLa\(_2\)Ti\(_3\)O\(_{10}\) compounds (M= Fe and Cu). The product retains a layered structure and is isostructural to both reported triple layered perovskites with a pattern very similar to that of the iron analogue. The pattern was indexed on a tetragonal unit cell and the lattice parameters are listed in Table B.1.

**Table B.1** Lattice parameters of FeLa\(_2\)Ti\(_3\)O\(_{10}\), Fe\(_{0.5}\)Cu\(_{0.5}\)La\(_2\)Ti\(_3\)O\(_{10}\) and CuLa\(_2\)Ti\(_3\)O\(_{10}\)

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeLa(_2)Ti(<em>3)O(</em>{10})</td>
<td>3.81460(9)</td>
<td>27.2893(9)</td>
</tr>
<tr>
<td>Fe(<em>{0.5})Cu(</em>{0.5})La(_2)Ti(<em>3)O(</em>{10})</td>
<td>3.7812(2)</td>
<td>27.1667(4)</td>
</tr>
<tr>
<td>CuLa(_2)Ti(<em>3)O(</em>{10})</td>
<td>3.8248(2)</td>
<td>26.329(1)</td>
</tr>
</tbody>
</table>

Fe\(_{0.5}\)Cu\(_{0.5}\)La\(_2\)Ti\(_3\)O\(_{10}\)’s unit cell is bigger than that of CuLa\(_2\)Ti\(_3\)O\(_{10}\) which was expected as Fe\(^{2+}\) ions are larger than Cu\(^{2+}\) (0.77 Å vs 0.71 Å).\(^{15}\) It is expected that bigger iron atoms present in the tetrahedral sites would dictate the interlayer space. FESEM images were taken to look at the morphology of the product (Figure B.2). As can been seen on the pictures, the plate-like morphology of the crystallites is comparable to that of FeLa\(_2\)Ti\(_3\)O\(_{10}\) (Figure 2.3). No structural
refinement has been carried out at this point but a random sharing of half of the tetrahedral sites in the interlayer in a structure similar to that of FeLa$_2$Ti$_3$O$_{10}$.

Figure B.1 X-ray diffraction patterns of (a) FeLa$_2$Ti$_3$O$_{10}$, (b) Fe$_{0.5}$Cu$_{0.5}$La$_2$Ti$_3$O$_{10}$ and (c) CuLa$_2$Ti$_3$O$_{10}$

Figure B.2 FESEM pictures of Fe$_{0.5}$Cu$_{0.5}$La$_2$Ti$_3$O$_{10}$
• **Thermal Behavior**

TGA-DSC characterization was run of Fe$_{0.5}$Cu$_{0.5}$La$_2$Ti$_3$O$_{10}$ up to 1000 °C under Ar and 800 °C under H$_2$/Ar. The TGA data for the measurement up to 800 °C are shown in Figure B.3, the data up to 1000 °C under inert atmosphere being too noisy to be reported.

![Figure B.3 TGA data for Fe$_{0.5}$Cu$_{0.5}$La$_2$Ti$_3$O$_{10}$ under (a) Ar and (b) H$_2$/Ar](image)

When heated under Ar, the compound undergoes a first weight loss up to 350 °C followed by a slight weight gain up to 400 °C before another small weight loss. TGA data for the heating under reducing atmosphere shows consecutive weight losses events. No clear thermal event was observed in the DSC signals with the exception of a small endotherm at 900 °C under Ar.
associated with a clear weight loss in the TGA data that may be correlated with a decomposition event. XRD patterns after analysis up to 800 °C are shown in figure B.4. The H₂ product appear isostructural with the triple layered perovskites as all the reflections are still present but additional peaks at 29.5 and 47 °2θ suggests that another phase in present in the sample.

![X-ray diffraction patterns](image)

**Figure B.4** X-ray diffraction patterns of TGA products under (a) Ar and (b) H₂/Ar at 800 °C compared to (c) Fe₀.₅Cu₀.₅La₂Ti₃O₁₀, (d) FeLa₂Ti₃O₁₀ and (c) CuLa₂Ti₃O₁₀

The compound obtained by heating under Ar up to 800 °C exhibit a pattern similar to that of Fe₀.₆₇La₂Ti₃O₁₀ as shown in Figure B.5. It is possible that similar oxidation of the iron atoms in the interlayer occurs but additional characterization would be necessary to rule out the possibility of a decomposition as the resulting pattern is also similar to that of La₂Ti₃O₇. Additionally, no evidence of Fe₂O₃ was found in the sample, visually (no red particles) or in the XRD pattern.
The magnetic behavior of FeLa$_2$Ti$_3$O$_{10}$ was presented in Chapter 2 as it exhibits a spin glass transition at 23 K. For comparison purpose, CuLa$_2$Ti$_3$O$_{10}$ was also characterized and exhibits a straight paramagnetic behavior. The calculated magnetic moment of 2.18 μ$_B$ is within the usual range for Cu$^{2+}$ ions (1.90 μ$_B$ theoretical). The ZFC-FC curves for FeLa$_2$Ti$_3$O$_{10}$, CuLa$_2$Ti$_3$O$_{10}$ and Fe$_{0.5}$Cu$_{0.5}$La$_2$Ti$_3$O$_{10}$ are presented in Figure B.6. In the case of the Fe$_{0.5}$Cu$_{0.5}$ compound, no magnetic transition is observed. A slight divergence of the ZFC and FC curves at low temperatures may be due to the instrument. A linear fit of the reciprocal susceptibility versus was obtained from 150 to 300 K, as a result of a Curie-Weiss paramagnetism. The calculated moment of 3.91 μ$_B$ is in good agreement with the theoretical value of 3.32 μ$_B$ for the contribution of both Fe$^{2+}$ and Cu$^{2+}$ ions. A small hysteresis loop is observed at 4 K but not at 20 K and above, where only a straight line is observed, consistent with the paramagnetic behavior at high temperatures.
According to the negative Weiss constant of -21.5 K, antiferromagnetic interactions are found in the sample. However, they are not as strong as those in FeLa$_2$Ti$_3$O$_{10}$. The copper present in the interlayer may have a “cancelling” effect on the antiferromagnetic behavior.

**Figure B.6** Magnetic susceptibility as a function of the temperature for (a) FeLa$_2$Ti$_3$O$_{10}$, (b) CuLa$_2$Ti$_3$O$_{10}$ and (c) Fe$_{0.5}$Cu$_{0.5}$La$_2$Ti$_3$O$_{10}$

**Figure B.7** Hysteresis loops at 4 (blue), 20 (red) and 300 K (green)
**B.4 Conclusions**

$\text{Fe}_{0.5}\text{Cu}_{0.5}\text{La}_2\text{Ti}_3\text{O}_{10}$ was successfully obtained by ion exchange reaction on the Ruddlesden-Popper phase $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ with $\text{FeCl}_2$ and $\text{CuCl}_2$ simultaneously at 350 °C under vacuum. The resulting compound is isostructural with $\text{FeLa}_2\text{Ti}_3\text{O}_{10}$ and exhibit paramagnetic behavior at temperatures as low as 20 K. Antiferromagnetic interactions are suggested based on the negative Weiss constant. This compound is the first example of dual ion exchange reaction where two transition metals are sharing the sites in the interlayer space.

**B.5 References**


VITA

The author was born in Niort, France. She graduated from Jean Macé high school in July 2007. She started her undergraduate studies at the University Institute of Technology (IUT) in Poitiers, France, where she received her two-year university degree in technology (DUT) in June 2009. She completed her B.S. degree in Chemistry in the spring of 2010 at Heriot Watt University, Edinburgh, Scotland and joined the Ph.D. program at the University of New Orleans in the fall of 2010. She was accepted in Prof. John B. Wiley’s research group in December 2010. In the spring of 2014, she received her M.S in Chemistry.