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Oxidation Chemistry of Some Early Transition-Metal Layered Perovskites

Karachie Ward
University of New Orleans

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OXIDATION CHEMISTRY OF SOME EARLY TRANSITION-METAL LAYERED
PEROVSKITES

A Thesis

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

Master of Science
in
The Department of Chemistry

by

Karachie Ward

B.S. Xavier University, 2001

May 2004

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Abstract

Early transition-metal oxyhalides, $(MCl)LaNb_2O_7$ ($M = V, Cr$) have been prepared by ion exchange of layered perovskite hosts, $ALaNb_2O_7$ ($A = Li, Rb$), with anhydrous metal halides, MCl_2 . These compounds contain low-valent metals (M^{2+}) that are receptive to oxidation. Thermogravimetric analysis (TGA) shows oxygen uptake at low temperatures (< 500 °C) and subsequent X-ray powder diffraction indicates that the host structure is maintained upon oxidation. Also through EDAX of the starting material and products, it has been found that there is a loss of chlorine upon oxidation. Thorough characterization of oxidation products will be presented and the ramifications of this chemistry on low-temperature topotactic formation of metal-oxide layers within perovskite hosts will be discussed

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Introduction

Perovskite compounds have been extensively studied in the past decade due to the great potential of the developmental properties of their structures. At the heart of their unique properties is their lattice geometry that consists of an octahedral interstice. These structures consist of 12-coordinated A^{+2} atoms on the corners of a cube, octahedral oxygen ions on the faces, and tetrahedral B^{+4} ions in the center.¹ The structure is capable of incorporating a large number of rare ores such as tantalum and niobium.² The general chemical formula for an oxide perovskite is ABO_3 .³ The name comes from the mineral $CaTiO_3$, which exhibits this structure. The following is the structure of $CaTiO_3$:⁴

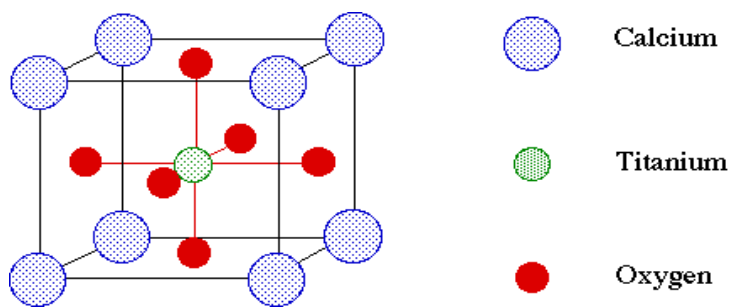


Figure 1: $CaTiO_3$

In this structure the calcium ions reside at the corners of the unit cell, while the titanium ion sits in the center of the cell surrounded by the oxygen ions located in the middle of each of the six planes.⁵ In this example, the central cation is the titanium ion, which causes a net dipole moment when it is displaced.⁶ This displacement of the central cation is what gives the perovskites their interesting properties.⁷

The physical properties of perovskite materials are diverse, including ferroelectric, piezoelectric, and superconducting properties that attract much interest in the material science field.⁸ The perovskite structure accommodates most of the metallic ions in the periodic table and a significant number of different anions.⁹ The majority of the perovskite compounds are oxides or fluorides, but the perovskite structure is also known for the heavier halides, sulfides, hydrides, cyanides, oxyfluorides and oxynitrides.¹⁰ These structures have the property that the central atom does not have contact with its coordination neighbors. This gives the structure the property of ferroelectricity. Possibly related to the structure's ferroelectricity is that many superconductors have the perovskite structure.¹¹

Superconductors are materials that have no resistance to the flow of electricity. Not only have the limits of superconductivity not been reached, but also the theories that explain superconductor behavior are constantly under review.¹² The 1-2-3 superconductor has a structure similar to the perovskite structure and has an observed superconductivity at 93 K. The resulting unit cell consists of three stacked cubic unit cells; it is considered to be orthorhombic rather than cubic, having an almost square base but rectangular sides.¹³

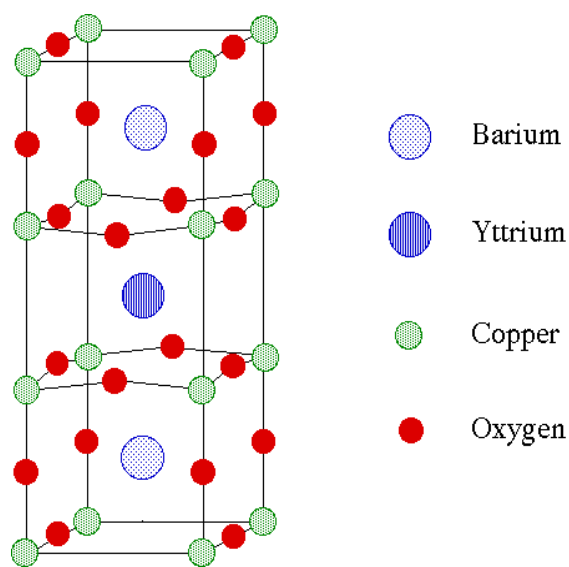


Figure 2: YBa₂Cu₃O_{7-x}

The development and research of this and many other pervoskite structures may lead to superconductors functioning at even higher temperatures, perhaps above 200K.¹⁴

Dion-Jacobson layered pervoskites have become of great interest due their topochemical manipulations, ion exchange,¹⁵ and intercalation properties.¹⁶ These A-site ordered compounds are of general formula $A'[A_{n-1} B_n O_{3n+1}]$ where A' = alkali metal, A = rare earth or alkali earth metal and B = transition metal and n = the number of pervoskite layers.^{17,18} The structures of Dion-Jacobson layered compounds are composed of two-dimensional slabs of corner-shared octahedra with the arrangement dependent upon the size of the A' cations in the inter-slab region.¹⁸ They contain A-site ordered cations and only one sheet of inter-slab A-cations.. A typical structure of these compounds is shown below:¹⁹

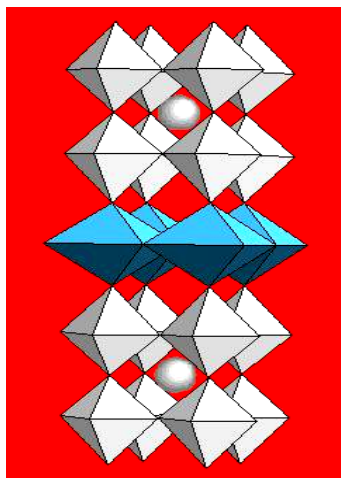


Figure 3: Structure of Dion-Jacobson compounds

The lower inter-slab alkali metal density promotes ion exchange compared to Ruddlesden-Popper compounds of general formula $A_2'[A_{n-1} B_n O_{3n+1}]$ which consist of an extra slab of inter-slab A-cations.²⁰ The coordination of these inter-slab A' -cations varies with the ionic radius of the alkali metal.²¹ This coordination increases from 4-fold for Li and Na, 6-fold for K, to 8-fold for Rb and Cs. Therefore the Li, Na, and K members occupy only 50% of the crystallographic A sites, while the Cs and Rb members are eight fold coordinated to the apical

oxygens of the Nb(Ta)O₆ octahedra with all the A sites occupied.²² The double-layered perovskites used for this research are RbLaNb₂O₇ and LiLaNb₂O₇.

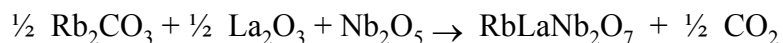
The ability of Dion-Jacobson compounds to be topochemically manipulated to achieve thermodynamically stable compounds has aroused great interest. A topochemical reaction is a reaction driven by the crystal structure rather than by the chemical nature of the reactants.²³ These compounds have been the subject of many investigations because of the ease in which ion exchange or intercalation occurs.²⁴ Ion exchange and intercalation are low temperature methods that are known to generate metastable compounds. These reactions are often reversible.²⁵ In ion exchange reactions, there is a weakly bonded species that can be substituted by another species. In intercalation reactions, there are ions or molecules being inserted within the layers.²⁶

The Dion Jacobson compounds have been demonstrated to coexchange both cations and anions to form (MX)LaNb₂O₇ compounds where M= first row transition metal and X = halide, usually, Cl.²⁷ In this research, early transition-metal oxyhalides, (MCl)LaNb₂O₇ (M = V, Cr) have been prepared by ion exchange of the layered perovskite hosts, ALaNb₂O₇ (A = Li, Rb), with anhydrous metal halides, MCl₂.²⁸ These compounds contain low-valent metals (M²⁺) that are receptive to oxidation. The synthesis and structural characterization upon oxidation of these (MCl)LaNb₂O₇ (M = V, Cr) will be presented.

Experimental

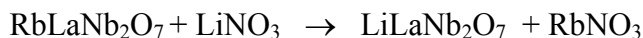
Synthesis of RbLaNb₂O₇ and LiLaNb₂O₇

The Dion Jacobsen perovskite host compound, RbLaNb₂O₇, was synthesized from Rb₂CO₃ (Alfa, 99%), La₂O₃ (Alfa, 99.99%) ,and Nb₂O₅ (Alfa, 99.9985%), by the following reaction:



Reaction 1

A 25 % molar excess of Rb₂CO₃ was used in order to accommodate for the loss of Rb₂O due to volatilization. La₂O₃ was heated for 24 hours at 1050° C in order to remove any carbonates or water impurities. The reactants were grinded and placed in a porcelain crucible and heated for 24 hours at 1050° C. It was then reground and heated for an additional 24 hrs at 1050 °C. The product was washed with distilled water and acetone to remove any excess impurities and dried at 100 °C for 10 hours. X-ray diffraction was used to confirm the presence of the desired product. Once RbLaNb₂O₇ was made an ion exchange reaction was performed on RbLaNb₂O₇ in order to make another similar perovskite host, LiLaNb₂O₇.^{20, 29}



Reaction 2

RbLaNb₂O₇ and anhydrous LiNO₃, in a 10:1 molar ratio, were grinded and placed in a porcelain crucible and heated for 24 hours at 300 °C.²⁹ The product was washed with warm distilled water and acetone in order to remove excess RbNO₃ from the compound. After the

product was dried at 100 °C for 12 hours, x-ray diffraction was used to confirm the ion exchange of the rubidium with lithium in the host compound. The following x-ray diffraction pattern shows $\text{RbLaNb}_2\text{O}_7$ and $\text{LiLaNb}_2\text{O}_7$:

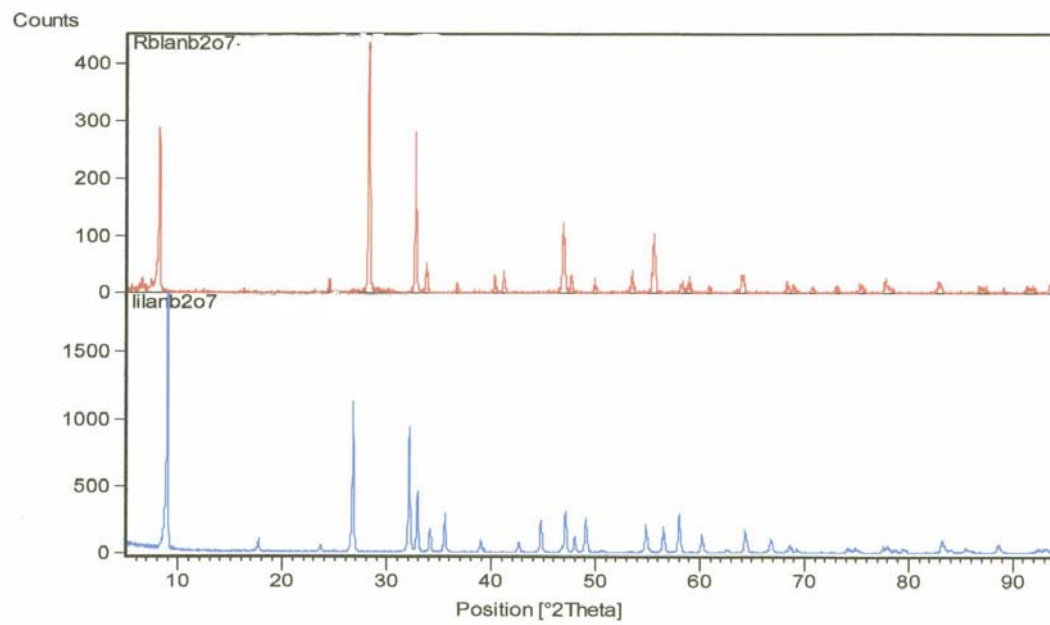


Figure 4: X-ray scan of $\text{RbLaNb}_2\text{O}_7$ and $\text{LiLaNb}_2\text{O}_7$

All powder x-ray diffraction data collected for this and further experiments were taken on a Philips X-Pert PW 3020 MPD X-ray diffractometer. It contains a graphite monochromator and $\text{Cu K}\alpha$ radiation with a wavelength of 1.5418 Å. A step-scanning mode was used between 5 and 95° at 2θ with a 10 s count time.

Synthesis of $(\text{MCl})\text{LaNb}_2\text{O}_7$

The $\text{RbLaNb}_2\text{O}_7$ and $\text{LiLaNb}_2\text{O}_7$ perovskites were used as the host compounds in order to prepare $(\text{MCl})\text{LaNb}_2\text{O}_7$ by an ion exchange reaction. The ion exchange reaction between the anhydrous transition metal halide and the double-layered perovskite can be shown as follows in figure 5: ²⁹

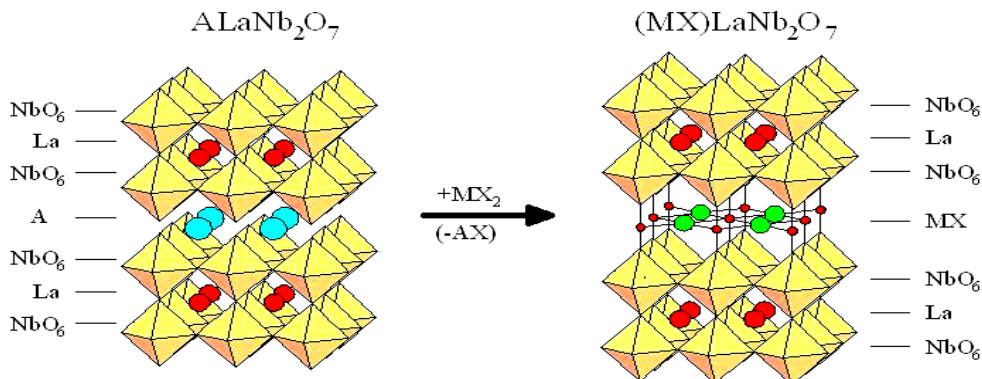
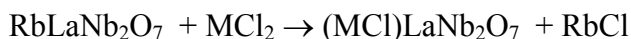


Figure 5: Ion-exchange Reaction

where A is the alkali metal (Li, Rb) and M is the transition metal (V, Cr) and X is the halide (Cl).

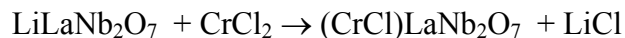
The specific reaction for making $(\text{CrCl})\text{La Nb}_2\text{O}_7$ and $(\text{VCl})\text{La Nb}_2\text{O}_7$ is shown as follows:



Reaction 3

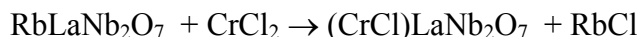
The metal chloride has to be anhydrous in order to prevent the oxidation of the transition metal.³⁰ In this case the transition metals used are vanadium and chromium. It was found that the CrCl_2 is extremely moisture sensitive compared to the VCl_2 , therefore careful attention was given to prevent these compounds from having exposure to air. The host compound and the metal chloride are combined in a 1:2 molar ratio. The mixture is ground and pressed into a pellet in an argon filled dry box. It is then sealed in an evacuated Pyrex tube and placed in a tube furnace for thermal treatment for approximately 6 to 14 days depending on the reactants. The products were washed in distilled water and/or absolute ethanol depending on the metal and dried at 100°C for 24 hours. X-ray data were then obtained in order to tell if successful reactions occurred.

$(\text{CrCl})\text{La Nb}_2\text{O}_7$ was prepared from $\text{LiLa Nb}_2\text{O}_7$ using CrCl_2 according to the following reaction³¹:



Reaction 4

Some of the starting material and unreacted CrCl_2 still existed in the final product according to the x-ray data. The following reaction was also attempted to make $(\text{CrCl})\text{LaNb}_2\text{O}_7$:



Reaction 5

Initial attempts to prepare $(\text{CrCl})\text{LaNb}_2\text{O}_7$ from $\text{RbLaNb}_2\text{O}_7$ were unsuccessful with the products consisting of unreacted starting materials. These attempts were made with x-ray data taken at various time periods between 6 to 14 days with little or no signs of a completed reaction after 2 weeks. A sample of the x-ray data from these attempts are shown below:

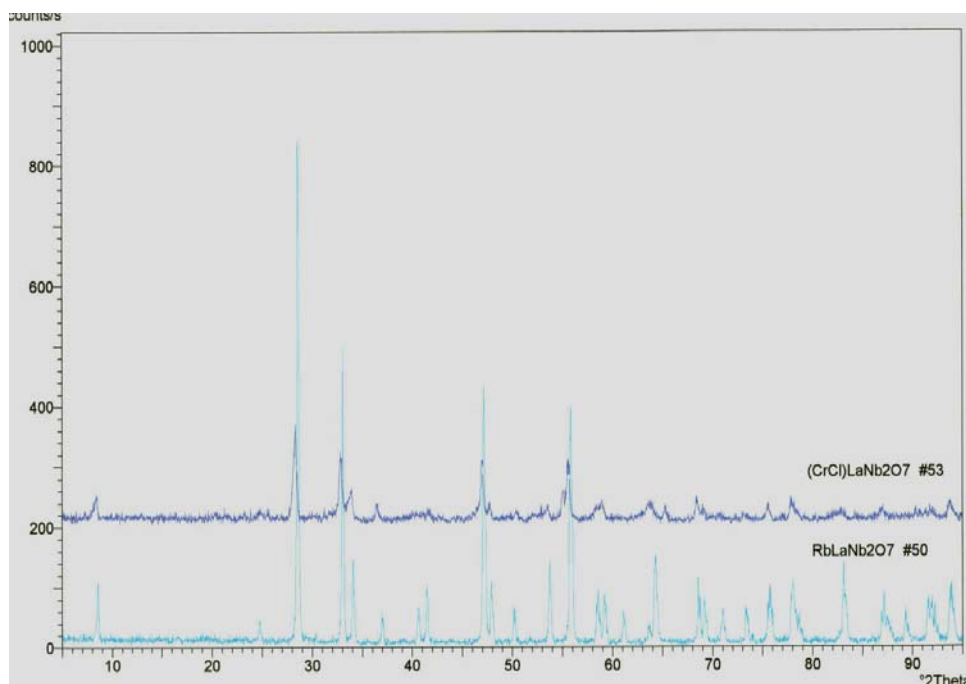


Figure 6: X-rays of $(\text{CrCl})\text{LaNb}_2\text{O}_7$ and $\text{RbLaNb}_2\text{O}_7$

The x-ray diffraction pattern for $(\text{CrCl})\text{LaNb}_2\text{O}_7$ contained the same peaks as $\text{RbLaNb}_2\text{O}_7$, which confirmed the unsuccessful reaction.

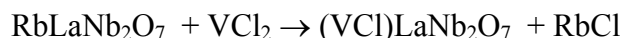
A variation in the temperature, time, and molar ratios were investigated in order to form a pure $(\text{CrCl})\text{LaNb}_2\text{O}_7$ product from $\text{LiLaNb}_2\text{O}_7$ and CrCl_2 . So far the best final product was achieved in 6 days at 420°C in a 1:2 molar ratio. At higher temperatures the reaction was faster but the product was contaminated with secondary phases. When the molar ratio of $\text{LiLaNb}_2\text{O}_7$ and CrCl_2 was increased to 1:3 the product mainly consisted of the unreacted starting materials. The estimated unit cells for $(\text{CrCl})\text{LaNb}_2\text{O}_7$ and the starting compound $\text{LiLaNb}_2\text{O}_7$ obtained from the x-ray data are shown in the following table:

	a	c
$(\text{CrCl})\text{LaNb}_2\text{O}_7$	3.8129 Å	11.1961 Å
$\text{LiLaNb}_2\text{O}_7$	3.7556 Å	10.0598 Å

Table 1: Unit cells for $(\text{CrCl})\text{LaNb}_2\text{O}_7$

As shown in the above table, there is a slight expansion in the unit cell in going from $\text{LiLaNb}_2\text{O}_7$ to $(\text{CrCl})\text{LaNb}_2\text{O}_7$ which contributes to the at least some of the reaction had taken place with the chromium cations being inserted between the apical oxygens of the perovskite blocks as was shown in figure 3.

$(\text{VCl})\text{LaNb}_2\text{O}_7$ could be prepared from $\text{RbLaNb}_2\text{O}_7$ and VCl_2 according to the following reaction¹⁹:



Reaction 6

Like $(\text{CrCl})\text{LaNb}_2\text{O}_7$, some of the starting materials and unreacted metal halide still existed in the final product in attempting to synthesize $(\text{VCl})\text{LaNb}_2\text{O}_7$. The best final product

was achieved in 7 days in a 1:2 molar ratio. A sample of the x-ray data for $(\text{VCl})\text{LaNb}_2\text{O}_7$ is shown below in figure 7:

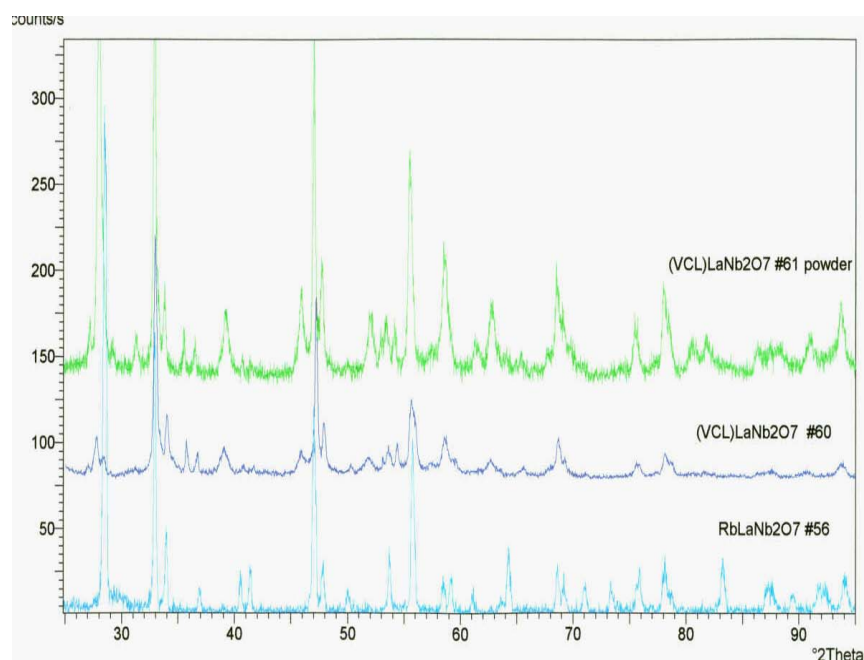


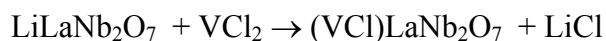
Figure 7: X-rays of $(\text{VCl})\text{LaNb}_2\text{O}_7$ and $\text{RbLaNb}_2\text{O}_7$

The reaction was attempted in an argon filled dry box with the reactants being grinded and pressed into pellets and left as a powder. Both forms of the reactants were evacuated and sealed in separate Pyrex tubes and heated in a tube furnace at various reaction times and temperatures. The above x-ray shows similar results obtained at 420°C in 7 days for both the powder and pellet forms of the reactants to obtain $(\text{VCl})\text{LaNb}_2\text{O}_7$. Both samples were washed with distilled water and ethanol and dried at 100°C for ~ 12 hours. The estimated unit cells obtained for $(\text{VCl})\text{LaNb}_2\text{O}_7$ and the starting compound $\text{RbLaNb}_2\text{O}_7$ from x-ray data are shown in the following table:

	a	c
(VCl)LaNb₂O₇	3.8783 Å	11.5561 Å
RbLaNb₂O₇	3.6057 Å	10.6525 Å

Table 2: Unit cells for (VCl)LaNb₂O₇ and RbLaNb₂O₇

Table 2 shows that there is a slight expansion in going from RbLaNb₂O₇ to (VCl)LaNb₂O₇. This contributes to that at least part of the reaction took place within the compound. (VCl)LaNb₂O₇ was also attempted to be made from LiLaNb₂O₇ in the following reaction:



Reaction 7

This produced results similar to what has been presented with best results occurring at 420°C in 6 days.

The stability and oxidizing ability of these compounds were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The (CrCl)LaNb₂O₇ and (VCl)LaNb₂O₇ compounds underwent TGA and DSC under an oxygen atmosphere. A TA Instruments Thermal Analyst-200 system was used with a temperature range varying between 25 to 800 °C. Also Energy Dispersive Spectroscopy, EDS, was also used to further characterize the TGA data. The ability of the (MCl)LaNb₂O₇ compounds to accommodate additional species within the perovskite layers were also tested.

The use of reductive intercalation of various metals such as Na, K, and Cs was performed on the best attained (CrCl)LaNb₂O₇ and (VCl)LaNb₂O₇ compounds. These reactions were performed using a 1:10 ratio of the (MCl)LaNb₂O₇ compounds and the metals. They were

prepared in a way to allow the metal to never actually touch the $(MCl)LaNb_2O_7$ compound in an argon filled dry box. The reactions took place in evacuated and sealed Pyrex tubes and underwent thermal treatment with allowed reaction times varying from 24 hours to 3 days.

Also a chlorine treatment on these compounds at room temperature was also performed using a continuous flow of chlorine to the $(MCl)LaNb_2O_7$ compounds with allowed reaction times varying between 1 to 24 hours. The chlorine treatment was done to test the ability of the $(MCl)LaNb_2O_7$ compounds to accommodate additional chlorine within the perovskite layers.

Differential Scanning Colorimetry (DSC) was also performed on the $(MCl)LaNb_2O_7$ samples in order to obtain information on their thermal stability. An oxygen and an argon gas flow was used on a Netzsch 404S thermal analysis system. Powder samples of the $(MCl)LaNb_2O_7$ was used and placed in alumina pans. The samples were heated at a rate of 10°C per minute.

Results and Discussion

Studies were done on the $(\text{CrCl})\text{LaNb}_2\text{O}_7$ and $(\text{VCl})\text{LaNb}_2\text{O}_7$ compounds in order to see if oxygen can be inserted within the layers of these compounds without the collapse of the overall structure. Thermogravimetric Analysis (TGA) was used in order to measure the change in weight of the compound as a function of temperature under an oxygen gas flow. The compound was heated from room temperature to $800\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}$ per minute with a continuous flow of oxygen to the compound. The following is a sample of a TGA for the $(\text{CrCl})\text{LaNb}_2\text{O}_7$ compounds.

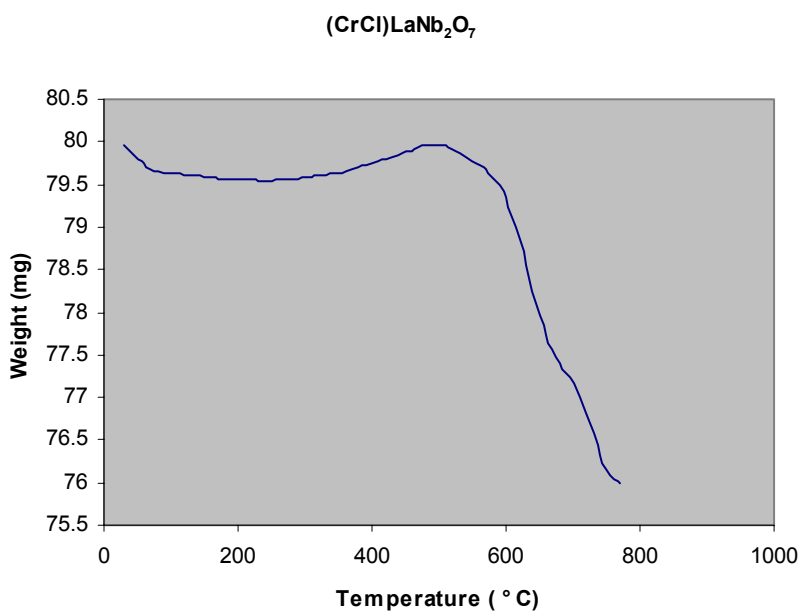


Figure 8: TGA for $(\text{CrCl})\text{LaNb}_2\text{O}_7$

As shown in the TGA data there is initially a small decrease in weight upon heating which may be due to a loss of water within the compound. The compound then maintains a steady weight until about 270 °C where it then starts to gain weight. Finally at 500 °C the compound has a steady weight loss due to the decomposition of the compound. This is supported by the XRD data taken at the end of the TGA experiment.

EDS, Energy Dispersive Spectroscopy, was used to try to determine what was contributing to the weight changes of the compound in the TGA results. EDS results were taken of the $(\text{CrCl})\text{LaNb}_2\text{O}_7$ compound before and after the TGA experiment. Also, isotherm TGAs were done at 300, 400, 500, and 600 °C in order to obtain a better understanding of what is happening in the chromium system upon heating under a oxygen gas flow. The following shows the chromium and chlorine content in the compound to the EDAX results at room temperature and after each isotherm TGA at the various temperatures:

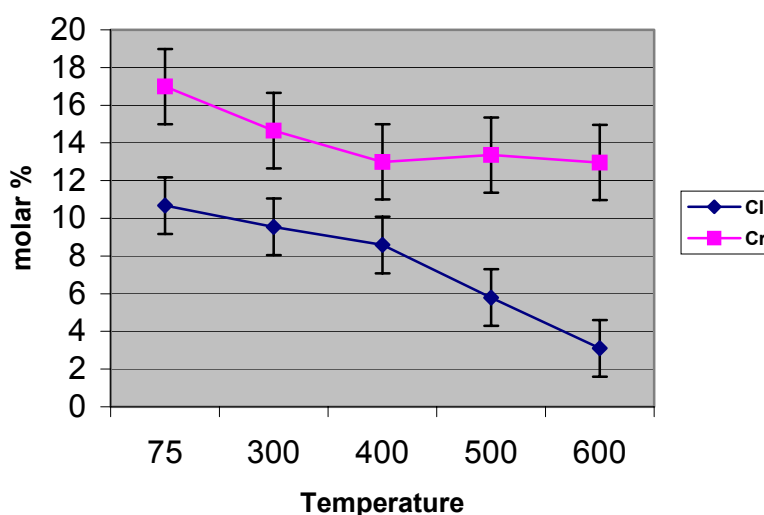
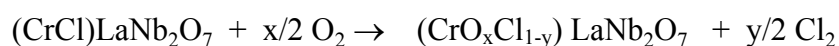


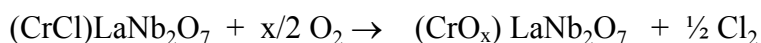
Figure 9: Chromium and Chlorine content in $(\text{CrCl})\text{LaNb}_2\text{O}_7$

The results show a significant loss in chlorine from the starting compound at room temperature with only ~5% of chlorine left in the compound upon completion of the isotherm TGA at 600°C. A possible explanation for this is that the oxygen is replacing the chlorine within the host structure. The chromium content decreased slightly in comparison to the content at room temperature and at 300° C. The chromium content was around the same amount for each of the isotherm TGAs at 300, 400, 500, and 600 °C when one takes into account possible error. These are promising results indicating that the host structure is being maintained throughout the TGA experiments. The following is the proposed reaction for the insertion of oxygen in the (CrCl)LaNb₂O₇ compound:



Reaction 8

It is also possible that the following reaction could also be occurring:



Reaction 9

In reaction 9, the oxygen has taken the place of all the chlorine within the compound. The EDS results favors reaction 8.

The vanadium system produced a much different TGA than the one for the chromium system as shown below:

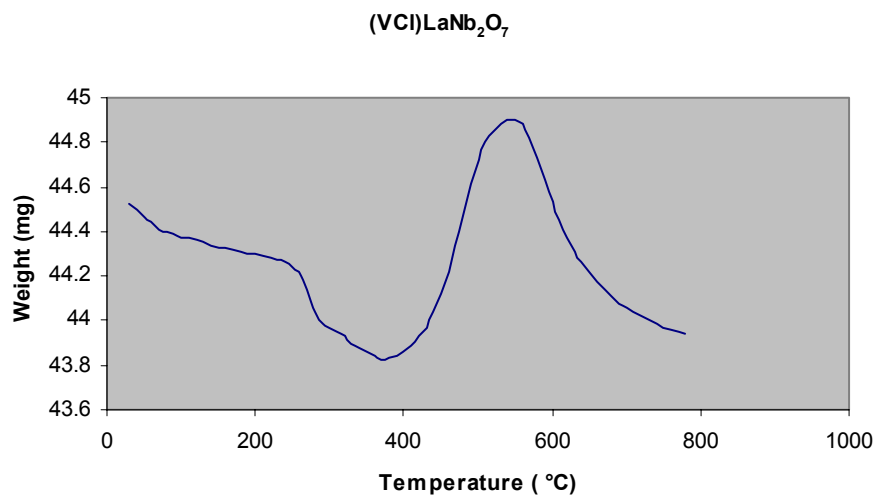
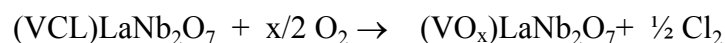


Figure 10: TGA of (VCl)LaNb₂O₇

There is a significant decrease in weight upon heating of the (VCl)LaNb₂O₇ until 380 °C. This decrease is then followed by a significant increase until the decomposition of the compound at 550 °C. EDS results show a depletion of all the chlorine in the (VCl)LaNb₂O₇ after the TGA. The following is the proposed reaction for this system:



Reaction 10

It was also noticed in the EDAX results a lost of vanadium in the compound upon heating. Isotherm TGAs at 300, 400, 500, and 600 °C were done in order to get a better understanding of what is happening in the vanadium system upon heating. EDAX were taken of each compound after each TGA experiment. The following shows the vanadium and chlorine content in the compound according to the EDAX results after each TGA:

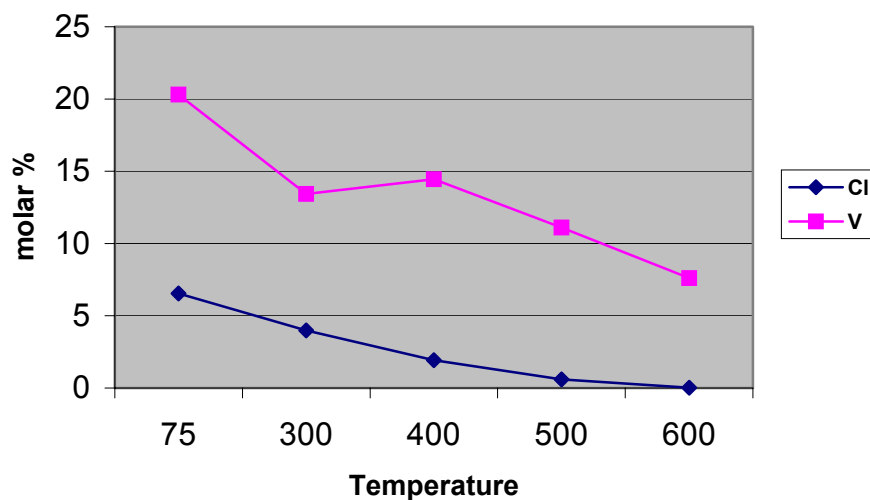
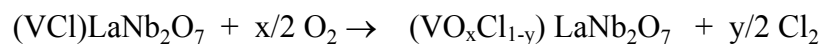


Figure 11: Vanadium and Chlorine content in (VCl)LaNb₂O₇

There is a loss of vanadium and chlorine in the compound as the temperature was increased.

There was a depletion of all the chlorine within the sample and a loss of ~ 63% of the vanadium within the compound during the isotherm TGA at 600 °C. Due to the EDS results the following reaction,



Reaction 11

may occur before the decomposition of the compound and the depletion of all the chlorine within its structure. Reaction 11 shows that chlorine remains in the (VCl)LaNb₂O₇ compound which is opposite from the data obtained from EDS after the isotherm TGA at 600 °C. This indicates that reaction 10 is the possible overall reaction for the thermogravimetric analysis of (VCl)LaNb₂O₇.

These results, along with the XRD data, indicates a collapse of the structure of the starting (VCl)LaNb₂O₇ compound. The following shows the XRD data of the compound at room temperature and after each isotherm TGA:

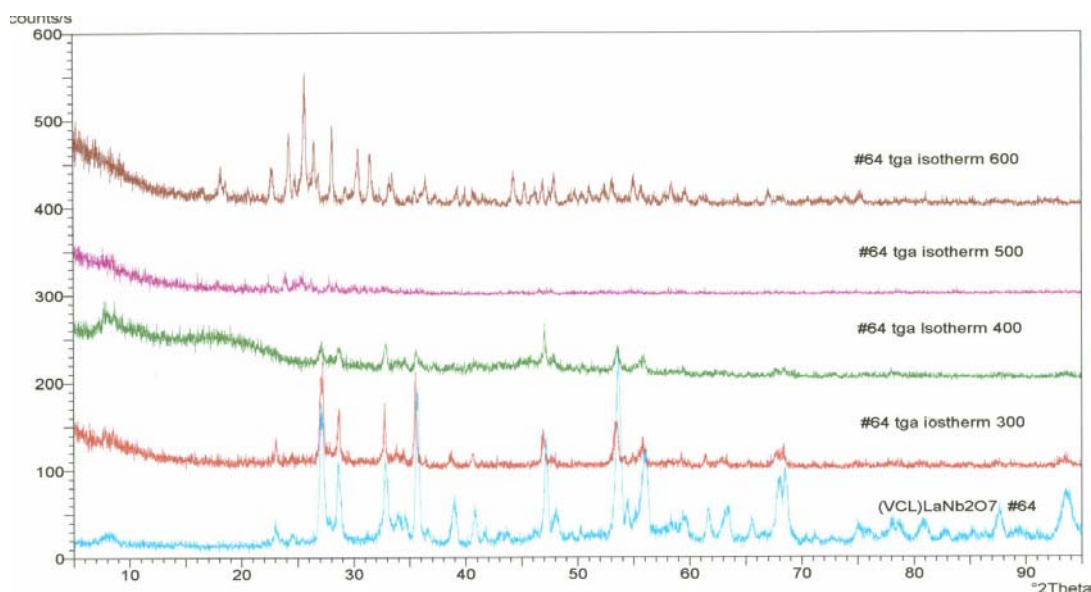


Figure 12: X-rays of (VCl)LaNb₂O₇ at various temperatures

As the temperature is increased there is a loss of peaks in the XRD data indicating a loss of crystallinity within the structure leading to its decomposition. In the XRD data for the isotherm TGA at 600 °C there is a reappearance of peaks possibly due to the formation of new compounds such as LaNb₂O₄ and VNbO₄. These results signify that the vanadium system is not a viable candidate for oxidative intercalation.

Further analysis was done on the chromium and vanadium systems in order to see if other species besides oxygen could be inserted within the layers. Thermogravimetric analysis was done on the (CrCl)LaNb₂O₇ and (VCl)LaNb₂O₇ compounds with argon as the flowing gas. All results produced show a steady decomposition of the structure as the temperature increased. Reductive intercalation with the metals Na, K, and Cs produced XRD results that were identical

to the starting compound. This indicated that these reactions were unsuccessful demonstrating that the is compound unable to accommodate these metals within its structure. Also chlorine treatment of the samples for 1, 3, and 6 hours at room temperature of the $(\text{CrCl})\text{LaNb}_2\text{O}_7$ and $(\text{VCl})\text{LaNb}_2\text{O}_7$ compounds also produced identical XRD results to the starting compound which also indicates that no reaction has taken place. The following figure shows the XRD data for the starting compound $\text{LiLaNb}_2\text{O}_7$, $(\text{CrCl})\text{LaNb}_2\text{O}_7$, $(\text{CrCl})\text{LaNb}_2\text{O}_7$ after chlorine treatment for 1 hour, and $(\text{CrCl})\text{LaNb}_2\text{O}_7$ after thermogravimetric analysis to 800°C :

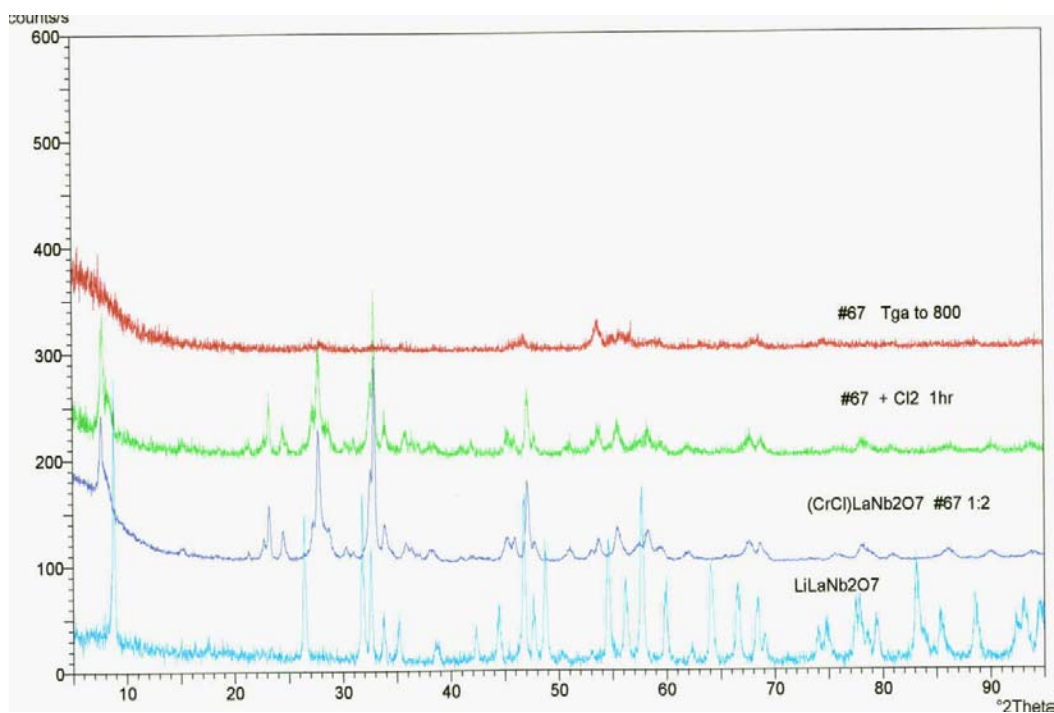


Figure 13: X-rays of $\text{LiLaNb}_2\text{O}_7$ and $(\text{CrCl})\text{LaNb}_2\text{O}_7$ after different experiments

These results show identical XRD data for $(\text{CrCl})\text{LaNb}_2\text{O}_7$ before and after chlorine treatment. In comparing the XRD results for $(\text{CrCl})\text{LaNb}_2\text{O}_7$ and the same compound after the thermogravimetric analysis to 800°C there is a loss of crystallinity. This indicates a decomposition of the $(\text{CrCl})\text{LaNb}_2\text{O}_7$ after the TGA experiment. The DSC measurements for the

(MCl)LaNb₂O₇ compounds showed exotherms at ~ 750 °C. It has been shown that these exothermic decompositions indicates that the (MCl)LaNb₂O₇ compounds are metastable²⁰.

Conclusions

The ability of Dion-Jacobson compounds to form metal-chloride networks with vanadium and chromium within the perovskite layers are promising. An improvement of synthesizing a pure $(\text{CrCl})\text{LaNb}_2\text{O}_7$ and $(\text{VCl})\text{LaNb}_2\text{O}_7$ systems is needed in order to further understand their properties and structural changes. Understanding the principles that control the formation and the stabilization of these compounds will allow for further development of new compounds with the same properties. The oxidation chemistry of the chromium system indicates the possibility of creating new compounds by the manipulation of the host structure. Also further analysis results show the host compound as very sensitive to the species that is trying to be inserted within the layers. This is most likely due to the size of the new species. The expansion of this oxidative chemistry to the second row transition metals is a possibility due to properties of the $(\text{CrCl})\text{LaNb}_2\text{O}_7$ compound.

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Vita

Karachie Harchie Ward was born in Laurel, Mississippi on May, 1979 and raised in Crowley, Louisiana. Her parents are both educators in the science field. They are her inspiration and provide her with inspiring insight for the future. She has one brother who is a junior at Morehouse college and one sister who is a freshman in high school. She graduated Church Point High school in May 1997 as class valedictorian. She obtained an undergraduate degree at Xavier University of New Orleans with a major in chemistry and a minor in biology. Her hobbies are reading, stamp collecting, and playing the piano. She plans on pursuing a career in scientific research.