Synthesis, crystal structure and ionic conductivity of ruddlesden-popper oxide materials: effects of ionic radii and defects on lithium-ionic conductivity.

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SYNTHESIS, CRYSTAL STRUCTURE AND IONIC CONDUCTIVITY OF
RUDDLESDEN-POPPER OXIDE MATERIALS: EFFECTS OF IONIC RADII AND
DEFECTS ON LITHIUM-IONIC CONDUCTIVITY

By

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M.S., East Tennessee State University, 2015

A Dissertation
Submitted to the Faculty of the
College of Arts and Sciences of the University of Louisville
in Partial Fulfilment of the Requirements
for the Degree of

Doctor of Philosophy in Chemistry

Department of Chemistry
University of Louisville
Louisville, Kentucky

December 2021
SYNTHESIS, CRYSTAL STRUCTURE AND IONIC CONDUCTIVITY OF RUDDLESDEN-POPPER OXIDE MATERIALS: EFFECTS OF IONIC RADII AND DEFECTS ON LITHIUM-IONIC CONDUCTIVITY

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A Dissertation Approved on

September 16th, 2021

by the following Dissertation Committee:

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DEDICATION

This work is dedicated to all members of the Seworh, Fanah, and the Bedu-Addo family for all the prayers and support. Lastly, I dedicate this work to the memory of my beloved father Mr. Solomon K. Seworh, and brother Albert Kevin Edem Fanah, who are no longer with us.
ACKNOWLEDGMENTS

Firstly, I want to thank God for the graciousness, mercies, and kindness he has caused to abound on me throughout my journey in graduate school. Not only has he been my rock, for he has been a shade and provided for me every step of the way. My earnest and deepest gratitude to my research supervisor and advisor Dr. Farshid Ramezanipour, who has been an irreplaceable mentor to me. It has been an honor to be part of the Ramezanipour research group. He has been an immense help, both consciously and unconsciously; his availability, guidance, counsel, support, patience, and most significantly his regard for his students is unrivaled. I appreciate him for not only allowing me to learn, nurture and develop into a better scientist, but also his desire to see all his students acquire the necessary skills to develop into better students.

To my family, I am grateful for all the prayers and support, which have helped me in the many difficult situations I found myself in throughout this graduate program. My profound gratefulness to my parents; Mr. Solomon K. Seworh, Mrs. Theresah Seworh, and Mad. Ruth Adjei for all their encouragement throughout my life. To my Pastors and shepherds, Rev. Harold Bedu-Addo and LP Dorothy Bedu-Addo, I am humbled and honored to have such great, amazing, loving, and caring people like yourself in my life. My journey through this program has been fruitful through consistent intercession, counsels, and encouragement. Also, I would like to appreciate my dear beautiful wife Dr. Grace Abban,
and my lovely daughters Selikem J. Fanah and Christabel F. Fanah, for being my bedrock, support, always inspiring me throughout this journey.

I would like to express my sincere thanks to Dr. Craig Grapperhaus, Dr. Richard Baldwin, and Dr. Gamini Sumanasekera for serving on my research and dissertation committee. My deepest regard and appreciation to all the kind people and staff at the Department of Chemistry for their academic and professional support; specifically, I would like to thank Mrs. Sherry Nalley for her selfless support to all graduate students in the Department. Last but not the least, I would like to thank all past and present members of Ramezanipour’s research group, for all the support and encouragement over my stay in the lab.
Layered perovskite oxides of the Ruddlesden-Popper (RP) type structure can be good lithium-ion conductors for solid electrolyte applications in all-solid-state batteries, due to the large gap separating octahedral layers which can be useful pathways for Li-ion conduction. However, little work has been done on their lithium-ion transport properties in these materials despite their interesting structural properties. This work highlights the synthesis and study of the ionic conductivities in a series of $n = 2$ and 3 Ruddlesden-Popper oxides, as part of an ongoing investigation in search of alternative solid electrolyte materials. Several different strategies were employed for the enhancement of the ionic conductivity in these materials.

To enhance the lithium-ion mobility in Li$_2$SrTa$_2$O$_7$, two hypotheses were explored: shortening Li-Li distances and inducing cation defects in the lithium layers. The first approach was carried out via the replacement of larger cations Sr$^{2+}$ and Ta$^{5+}$ with smaller cations La$^{3+}$ and Ti$^{4+}$. The resulting materials Li$_2$La(TaTi)O$_7$ and Li$_2$La(NbTi)O$_7$ are $n = 2$ RP materials showing higher magnitudes of conductivity than those reported for
Li$_2$SrTa$_2$O$_7$. Next, Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ and Li$_{1.8}$La(Nb$_{1.2}$Ti$_{0.8}$)O$_7$ which were made using the second strategy produced even higher values of conductivities. In addition, the two lithium-deficient materials demonstrated measurable conductivities at room temperature. A feature that was lacking in Li$_2$La(TaTi)O$_7$ and Li$_2$La(NbTi)O$_7$, as well as Li$_2$SrTa$_2$O$_7$. Given the improvement in conductivity due to cation deficiencies, the role of structural deficiencies in the form of defects at various sites in the RP structure was expanded to $n = 3$ members in subsequent projects. This was done in the studies of materials of the series Li$_{2-x}$La$_{2-y}$Ti$_{3-z}$Nb$_z$O$_{10}$, where defects were created in inter- or intra-layer sites, i.e., A or A'. A systematic increase in conductivity that trails the degree of defects were observed in materials with deficiencies at only lithium or lanthanum sites. Further studies showed that the simultaneous incorporation of defects at A and A' in the synthesis of Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$ greatly impacts the conductivity in these materials, even in cases where the degree of cation-deficiency on both inter- and intra-layer sites is similar or lesser than those in compounds containing defects on only one of the two sites. These results demonstrate for the first time that ionic transport in triple-layered Ruddlesden-Popper oxides is a result of the cooperative effect of both inter- and intra-layer sites, i.e., A and A.

Finally, the effects of cationic size (ionic radii) on lithium-ion mobility in RP materials were also explored through the synthesis of a series of three-layered materials such as Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$, and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. Diffraction experiments showed all three materials feature supercells ($\sqrt[3]{2a} \times \sqrt[3]{2b} \times \sqrt[3]{c}$), which are two times larger than typical unit cell volumes of RP oxides. The formation of supercells is directly enhanced lithium-ion conductivity of these materials as compared with their Sr-analogue, Li$_2$Sr$_{1.5}$Nb$_3$O$_{10}$, which lacks the supercell. Supplementary experiments on other triple
layered series featuring the same super cells confirmed that changes associated with symmetry effects in these materials play crucial roles on the overall impact on ionic mobility. These studies further highlight that the size of ions within the material structure can re-enforce or oppose parameters such as Li-Li distances, grain size, and grain contact in relation to the overall conductivity of these materials. A comparison between \( \text{Li}_2\text{SrLaTaTi}_2\text{O}_{10} \), \( \text{Li}_2\text{Sr}_2\text{Ta}_2\text{TiO}_{10} \), \( \text{Li}_2\text{CaLaTaTi}_2\text{O}_{10} \), and \( \text{Li}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{10} \) show that smaller cation sizes re-enforce the overall symmetry towards enhanced conductivity whiles the larger cations oppose the overall mobility in these material types.
TABLE OF CONTENTS

DEDICATION .................................................................................................................. iii

ACKNOWLEDGMENTS .................................................................................................. iv

ABSTRACT ...................................................................................................................... VI

CHAPTER 1 ...................................................................................................................... 1

INTRODUCTION ............................................................................................................ 1

1. Background ............................................................................................................. 1

1.1 Battery Components ........................................................................................... 4

1.1.1 Anode .............................................................................................................. 4

1.1.2 Cathode .......................................................................................................... 5

1.1.3 Electrolyte ...................................................................................................... 6

1.1.3.1 Liquid Electrolyte .................................................................................. 7

1.1.3.2 Solid Electrolyte .................................................................................... 7

1.2 Defects in Solid Materials .................................................................................. 9

1.2.1 Intrinsic Defects .......................................................................................... 11

1.2.2 Extrinsic Defects ......................................................................................... 12
1.3 Conductivity .................................................................................................................. 13

1.3.1 Electrical Conductivity .......................................................................................... 13

1.3.2 Electronic Conductivity ......................................................................................... 15

1.3.3 Ionic Conductivity ............................................................................................... 20

1.4 Chemical Diffusion .................................................................................................. 22

1.5 Experimental Techniques ......................................................................................... 24

1.6 Material Synthesis ................................................................................................... 25

1.6.1 Characterization Technique of Solid-State Materials ......................................... 26

1.6.1.1 Powder Diffraction ......................................................................................... 26

1.6.1.2 Bragg Equation .............................................................................................. 27

1.6.1.3 Neutron Powder Diffraction .......................................................................... 28

1.6.1.4 Electrical Conductivity Characterizations .................................................. 29

1.6.1.5 AC Impedance Spectroscopy ......................................................................... 29

1.7 Perovskites Oxides .................................................................................................. 35

1.7.1 Perovskite Structure ............................................................................................ 35

1.7.2 Layered Perovskite Oxides: Ruddlesden-Popper Structure ............................... 37

1.8 Ruddlesden-Popper Oxides as Potential Solid Electrolyte .................................. 39

CHAPTER 2 ......................................................................................................................... 44

INSIGHT INTO LITHIUM-ION MOBILITY IN Li2La(TaTi)O7 ........................................... 44
2.1 Experimental and Computational Methods ...........................................44
2.2 Results and Discussion ........................................................................46
2.3 Crystal Structure ..................................................................................46
2.4 Lithium-ion Conductivity ......................................................................50
2.5 Density Functional Theory Calculations ..............................................56
2.6 Conclusions .........................................................................................60

CHAPTER 3 ..............................................................................................61
ENHANCING THE LITHIUM-ION CONDUCTIVITY IN Li$_2$SrTa$_{2-x}$Nb$_x$O$_7$ (x = 0 - 2) ..........................................................61
3.1 Experimental .........................................................................................61
3.2 Results and Discussion ..........................................................................61
3.3 Crystal Structure ..................................................................................61
3.4 Ionic Conductivity .................................................................................67
3.5 Conclusions ..........................................................................................71

CHAPTER 4 ..............................................................................................73
EXPERIMENTAL AND THEORETICAL INVESTIGATION OF LITHIUM-ION CONDUCTIVITY IN Li$_2$LaNbTiO$_7$ ..................................73
4.1 Experimental .........................................................................................73
4.2 Results and Discussion ..........................................................................73
4.3 Crystal Structure ..................................................................................73
4.4 Ionic Conductivity .................................................................77
4.5 Density Functional Theory Calculations ..................................88
4.6 Conclusions ............................................................................91

CHAPTER 5 .........................................................................................92

STRATEGIES FOR ENHANCING LITHIUM-ION CONDUCTIVITY OF TRIPLE-
LAYERED RUDDLESDEN-POPPER OXIDES: CASE STUDY OF Li$_{2-x}$La$_{2-y}$Ti$_{3-z}$Nb$_z$O$_{10}$
...........................................................................................................92

  5.1 Experimental ...........................................................................92
  5.2 Results and Discussion ..............................................................93
  5.3 Crystal Structure ......................................................................93
  5.4 Ionic Conductivity ....................................................................99
  5.5 Frequency-Dependent Impedance and Dielectric Analyses ..........106
  5.6 Conclusions ............................................................................111

CHAPTER 6 ..........................................................................................113

LITHIUM-ION MOBILITY IN LAYERED OXIDES Li$_2$Ca$_{1.5}$Nb$_{3}$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$
AND Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$, ENHANCED BY SUPERCELL FORMATION ..........113

  6.1 Experimental ...........................................................................113
  6.2 Results and Discussion ..............................................................114
  6.3 Crystal Structure ......................................................................114
  6.4 Ionic Conductivity ....................................................................120
6.5 Frequency-Dependent Impedance, Dielectric and Complex Modulus Analyse..........................................................................................................................125

6.6 Conclusions.................................................................................................................................130

CHAPTER 7 ..................................................................................................................................132

SYMMETRY EFFECT ON THE ENHANCEMENT OF LITHIUM-ION MOBILITY IN LAYERED OXIDES Li$_2$A$_2$B$_2$TiO$_{10}$ (A = La, Sr, Ca; B = Ti, Ta) ..................................................132

7.1 Experimental ..............................................................................................................................132

7.2 Results and Discussion ..............................................................................................................133

7.3 Crystal Structure .......................................................................................................................133

7.4 Ionic Conductivity .....................................................................................................................140

7.5 Frequency-Dependent Impedance .............................................................................................145

7.6 Dielectric and Loss Tangent Analyses.......................................................................................149

7.7 Complex Modulus Analysis ......................................................................................................152

7.8 Conclusions .............................................................................................................................155

CHAPTER 8 ..................................................................................................................................156

CONCLUSION ..................................................................................................................................156

REFERENCES .................................................................................................................................160

CURRICULUM VITAE .....................................................................................................................169
LIST OF FIGURES

Figure 1.1: Schematic representation of charge/discharge process in a lithium-ion battery. ......................................................................................................................................................4

Figure 1.2.1: Representation of intrinsic defects in compound composition type MX. a) Schottky defect b) Frenkel defect. ........................................................................................................................................12

Figure 1.3.1: Band structure of a metal .............................................................................................................................16

Figure 1.3.2: Band structure of an insulator .....................................................................................................................16

Figure 1.3.3: Band structure of a semiconductor ...............................................................................................................17

Figure 1.3.4: Positive and negative charge carriers in semiconducting solids. ..........18

Figure 1.3.5: Types of semiconductors. a) p-type semi conductivity in gallium-doped silicon. b) n-type semi conductivity in arsenic-doped silicon.................................................................19

Figure 1.3.6: Temperature dependence of a) carrier concentration of semiconductor materials. b) conductivity of semiconductor materials. .................................................................20

Figure 1.3.7: Ion hopping mechanism in ionic solids..................................................................................................................21

Figure 1.4.1: A graphical representation of Bragg’s law.........................................................................................................28

Figure 1.5.1: Variation of current as a function of time in electronic, ionic, and mixed ionic/electronic conductors. .................................................................................................................. 32

Figure 1.5.2: Resistance-capacitance circuit units describing electrical contributions from different components of a material. ............................................................................................ 32

Figure 1.5.3: Representative Impedance plot of a polycrystalline material. ............... 34
Figure 1.6.1: Ideal cubic perovskite oxide structure a) unit cell with A and B cations shown in green and white with oxide ions in red. b) shows corner-shared BO$_6$ octahedra and 12-coordinated A-site cations respectively. c) Three-dimensional arrangement

Figure 1.7.1: Rudlesden-Popper materials showing different layers

Figure 2.1: Crystal structure of Li$_2$La(TaTi)O$_7$ (left) and the tetrahedral coordination of lithium atoms (right). Green, blue, gray, and red spheres show La, Ta/Ti, Li, and O, respectively.

Figure 2.2: Rietveld refinement profile for powder X-ray diffraction data (a) Li$_2$La(TaTi)O$_7$ in Cmcm space group. (b) Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ in I4/mmm space group. The black crosses represent experimental data, the red line shows the fit, vertical tick marks.

Figure 2.3: Neutron diffraction Rietveld refinement profile for Li$_2$La(TaTi)O$_7$ in Cmcm space group.

Figure 2.4: Scanning electron microscopy data for (a) Li$_2$La(TaTi)O$_7$ and (b) Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$.

Figure 2.5: Nyquist Impedance plots for Li$_2$La(TaTi)O$_7$.

Figure 2.6: Typical fit to Nyquist Impedance plot for Li$_2$La(TaTi)O$_7$ at 200 °C.

Figure 2.7: Nyquist Impedance plots for Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$.

Figure 2.8: Typical fit to Nyquist Impedance plot for Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ at 100 °C.

Figure 2.9: Arrhenius plots for Li$_2$La(TaTi)O$_7$ (red) and Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ (blue).

Figure 2.10: DFT optimized structures for Li$_2$La(TaTi)O$_7$ and their corresponding total energy per unit cell. The top left configuration has the lowest energy. Gray and blue octahedra represent TaO$_6$ and TiO$_6$. Lithium atoms are shown as small spheres between.
**Figure 2.11:** Calculated electronic band structure (left panel) and DOS (right panel) of the optimized Li$_2$La(TaTi)O$_7$ structure. The red dashed line indicates the Fermi energy, and the insert is the Brillouin zone with special high symmetry k points. ............................58

**Figure 2.12:** Energy barrier as a function of displacement of Li atoms from their original sites. The insets show the structures at maximum and minimum energy barriers. ............................59

**Figure 3.2:** Rietveld refinement profiles of powder X-ray diffraction data for (a) Li$_2$SrTa$_2$O$_7$ (b) Li$_2$SrNbTaO$_7$ and (c) Li$_2$SrNb$_2$O$_7$. Black crosses, red line, vertical tick marks, and lower blue line represent experimental data, the fit, Bragg peak positions, and the difference plot, respectively. .................................................................62

**Figure 3.3:** Typical SEM images of sintered pellets of Li$_2$SrTa$_2$O$_7$, Li$_2$SrTaNbO$_7$ and Li$_2$SrNb$_2$O$_7$. ........................................................................................................65

**Figure 3.4:** Rietveld refinement profiles of (a) X-ray and (b) neutron diffraction data for Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$. Black crosses, red line, vertical tick marks, and lower blue line represent experimental data, the fit, Bragg peak positions, and the difference plot, respectively. .................................................................65

**Figure 3.5:** Typical fits to the Nyquist impedance plots at 200 °C (upper panels) and 300 °C (lower panels). ........................................................................................................68

**Figure 3.6:** Typical fits to the Nyquist impedance plots for Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$. ..........69

**Figure 3.7:** Arrhenius plots for all compounds. The activation energies obtained from this plot are 0.69, 0.85, 0.64 and 0.44 eV for Li$_2$SrTa$_2$O$_7$, Li$_2$SrNbTaO$_7$, Li$_2$SrNb$_2$O$_7$ and Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$, respectively. .................................................................71

**Figure 4.1:** (a) Crystal structure of Li$_2$LaNbTiO$_7$. Blue, gray, and yellow spheres represent La, Nb/Ti, and Li, respectively. (b) The tetrahedral coordination environment of lithium. ........................................................................................................74

**Figure 4.2:** Rietveld refinement profile for Li$_2$LaNbTiO$_7$ in Cmcm space group. (a) Powder X-ray diffraction data. (b) Neutron diffraction data. The experimental data are represented by black crosses. The red line shows the fit, the vertical tick marks represent Bragg peak positions, and the lower blue line is the difference plot. .................................................................75
Figure 4.3: Scanning electron microscopy images of Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$. .................................................................................................................................77

Figure 4.4: Typical Nyquist Impedance plots for Li$_2$LaNbTiO$_7$. ..................................................78

Figure 4.5: Typical Nyquist Impedance plots for Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.................................79

Figure 4.6: Arrhenius plot for Li$_2$LaNbTiO$_7$ (black squares) and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ (blue triangles). .................................................................................................................................82

Figure 4.7: Real part of impedance data as a function of angular frequency (Z’ vs log ω) for (a) Li$_2$LaNbTiO$_7$ and (b) Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$...........................................................................................................................................83

Figure 4.8: Imaginary part of impedance data as a function of angular frequency (Z’’ vs log ω) for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$...........................................................................................................................................84

Figure 4.9: Temperature and frequency dependence of (a) dielectric constant (ε’) and (b) dielectric loss (tan δ) for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$. .................................................................85

Figure 4.10: Complex Modulus Plots for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$. .........87

Figure 4.11: Variations of real (M’) and imaginary (M’’) parts of Modulus with temperature over different frequency ranges for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.................................88

Figure 4.12: Calculated electronic band structure and density of states (DOS) for Li$_2$LaNbTiO$_7$. The red dashed line shows the Fermi energy. The Brillouin zone with special high symmetry k points is shown in the inset. .................................................................90

Figure 4.13: Energy barrier as a function of lithium displacement in b-direction for Li$_2$LaNbTiO$_7$ (black circles) and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ (red squares). The insets show the structures at the maximum and minimum energies. .................................................................91

Figure 5.1: Crystal structure of triple-layered Ruddlesden-Popper oxide, A$_2$A’$_2$B$_3$O$_{10}$ (A = Li, A’=La, B = Ti/Nb). (a) The BO$_6$ octahedra are shown in green, with blue and yellow spheres representing La and Li, respectively. (b) The LaO$_{12}$ and LiO$_4$ polyhedral are shown in blue and purple, respectively. .................................................................93
Figure 5.2: X-ray photoelectron spectroscopy data for Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$. The binding energies are consistent with trivalent lanthanum (a), pentavalent niobium (b), and tetravalent titanium (c). .......................................................... 94

Figure 5.3: Rietveld refinement profiles using X-ray diffraction data in I4/mmm space group for: (a) Li$_2$La$_2$Ti$_3$O$_{10}$. (b) Li-deficient compounds Li$_{1.9}$La$_2$Ti$_{2.9}$Nb$_{0.1}$O$_{10}$, Li$_{1.8}$La$_2$Ti$_{2.8}$Nb$_{0.2}$O$_{10}$, and Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$. (c) La-deficient compounds, Li$_2$La$_{1.9}$Ti$_{2.7}$Nb$_{0.3}$O$_{10}$ and Li$_2$La$_{1.8}$Ti$_{2.4}$Nb$_{0.6}$O$_{10}$. (d) Both Li- and La-deficient compound, Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. .......................................................... 98

Figure 5.4: Neutron refinement profiles for the two highly deficient compounds: (a) Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$ and (b) Li$_2$La$_{1.8}$Ti$_{2.4}$Nb$_{0.6}$O$_{10}$. .......................................................... 101

Figure 5.5: Impedance fits for all materials: (a) Li$_2$La$_2$Ti$_3$O$_{10}$. (b) Li-deficient compounds Li$_{1.9}$La$_2$Ti$_{2.9}$Nb$_{0.1}$O$_{10}$, Li$_{1.8}$La$_2$Ti$_{2.8}$Nb$_{0.2}$O$_{10}$, and Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$. (c) La-deficient compounds Li$_2$La$_{1.9}$Ti$_{2.7}$Nb$_{0.3}$O$_{10}$ and Li$_2$La$_{1.8}$Ti$_{2.4}$Nb$_{0.6}$O$_{10}$. (d) Both Li- and La-deficient compound, Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. .......................................................... 105

Figure 5.6: Arrhenius plots for all compounds. (a) Plot of Li$_2$La$_2$Ti$_3$O$_{10}$ with all lithium deficient compounds. (b) Plots of Li$_2$La$_2$Ti$_3$O$_{10}$ with all lanthanum deficient and a combination of lithium and lanthanum deficient compounds.............................................. 109

Figure 5.7: (a) Variation of real components of impedance as a function of frequency (Z’ vs logω) of Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. (b) Variation of the imaginary component of impedance as a function of frequency (Z’’ vs logω) of Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. .......................................................... 119

Figure 5.8: (a) Variation of dielectric constant a function of frequency of Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. (b) Variation tangent loss a function of frequency of Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. .......................................................... 111

Figure 6.1: (a) Crystal structure of a three-layer Ruddlesden-Popper oxide, A$_2$A’$_2$B$_3$O$_{10}$, where BO$_6$ octahedra are shown in green, intra-stack A-cations as blue spheres, and inter-stack A’-cations as small purple spheres. (b) Coordination geometry and connectivity of lithium ions. .......................................................... 114

Figure 6.2: Comparison between neutron diffraction refinements with I4/mmm and P4/z/nm for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$. Stars mark the peaks that do not match I4/mmm. ............. 116
Figure 6.3: (a) Rietveld refinements with powder X-ray diffraction for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$ in $P4_2/ncm$. (b) Rietveld refinements with neutron diffraction data for the two end members of the series, Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$ in $P4_2/ncm$. The experimental data, the model, Bragg peak positions, and the difference plot are represented by black crosses, red lines, vertical tick marks, and the lower blue line, respectively.

Figure 6.4: Scanning electron microscopy images showing the microstructures (a) Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, (b) Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and (c) Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. 

Figure 6.5: Typical impedance fits for (a) Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, (b) Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and (c) Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$, at 25 and 100°C.

Figure 6.6: Arrhenius plots Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

Figure 6.7: X-ray diffraction data before and after heating to 800°C in air, indicating excellent stability.

Figure 6.8: Variation of real ($Z'$) and imaginary ($Z''$) components of impedance as a function of angular frequency in (a) Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, (b) Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and (c) Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

Figure 6.9: Variation of dielectric constant($\varepsilon'$) and loss tangent (tan δ) as a function of angular frequency in Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

Figure 6.10: Complex modulus for (a) Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, (b) Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and (c) Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

Figure 7.1: (a) Crystal structure of Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta). (b) The AO$_{12}$, LiO$_4$ and (Ta/Ti)O$_6$ units are shown in green, purple and blue, respectively.

Figure 7.2: (a-e) Rietveld refinement profiles using X-ray diffraction data for Li$_2$La$_2$Ti$_3$O$_{10}$ ($I4/mmm$), Li$_2$SrLaTaTi$_2$O$_{10}$, Li$_2$Sr$_2$Ta$_2$TiO$_{10}$, Li$_2$CaLaTaTi$_2$O$_{10}$, and Li$_2$Ca$_2$Ta$_2$TiO$_{10}$ ($P4_2/ncm$). (f) Neutron diffraction data for Li$_2$Ca$_2$Ta$_2$TiO$_{10}$.
Figure 7.3: X-ray photoelectron spectroscopy data for the most conductive material, Li$_2$Ca$_2$Ta$_2$TiO$_{10}$. Binding energies (eV) are consistent with pentavalent tantalum and tetravalent titanium. .................................................................139

Figure 7.4: (a-e) Scanning electron microscopy images showing the microstructures of Li$_2$La$_2$Ti$_3$O$_{10}$, Li$_2$SrLaTaTi$_2$O$_{10}$, Li$_2$Sr$_2$Ta$_2$TiO$_{10}$, Li$_2$CaLaTaTi$_2$O$_{10}$ and Li$_2$Ca$_2$Ta$_2$TiO$_{10}$. ......................................................................................139

Figure 7.5: Impedance fits for all five materials at 200 °C ..................................................143

Figure 7.6: Arrhenius plots for all five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta). ..................................................................................................................145

Figure 7.7: Variation of the real component of impedance as a function of frequency (Z’ vs logω) for all five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta). .............147

Figure 7.8: Variation of the imaginary component of impedance as a function of frequency (Z” vs logω) for all five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta). ............148

Figure 7.9: Variation of dielectric constant (ε’) as a function of frequency for all five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta). .................................................................150

Figure 7.10: Variation of tangent loss (tan δ) as a function of frequency for all five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta). .................................................................151

Figure 7.11: Complex modulus and its variation function with frequency. Each row shows the data for one of the five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta).......154
LIST OF TABLES

Table 2.1: Refined structural parameters from Rietveld refinement with powder neutron diffraction data for Li$_2$La(TaTi)O$_7$. Space group $Cmcm$, $a = 18.2384(5)$ Å, $b = 5.5126(2)$ Å, $c = 5.4996(2)$ Å.

Table 2.2: Refined structural parameters from Rietveld refinement with powder X-ray diffraction data for Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$. Space group: $I4/mmm$, $a = 3.8986(0)$ Å, $c = 18.4520(3)$ Å.

Table 2.3: Variable temperature conductivity of Li$_2$La(TaTi)O$_7$ and Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$.

Table 3.1: Refined structural parameters from powder X-ray diffraction data for Li$_2$SrTa$_2$O$_7$. Space group $Cmcm$, $a = 18.1928(2)$ Å, $b = 5.5860(1)$ Å, $c = 5.5807(1)$ Å, Volume = 567.14(1) Å$^3$, $Rwp = 0.1134$, $Rp = 0.0846$.

Table 3.2: Refined structural parameters from powder X-ray diffraction data for Li$_2$SrNb$_2$O$_7$. Space group $Cmcm$, $a = 18.0004(4)$ Å, $b = 5.5994(2)$ Å, $c = 5.5938(2)$ Å, Volume = 563.80(3) Å$^3$, $Rwp = 0.0945$, $Rp = 0.0711$.

Table 3.3: Refined structural parameters from Powder X-ray diffraction data for Li$_2$SrNbTaO$_7$. Space group $Cmcm$, $a = 18.1038(2)$ Å, $b = 5.5934(1)$ Å, $c = 5.5863(1)$ Å, Volume = 565.68(1) Å$^3$, $Rwp = 0.1112$, $Rp = 0.0820$.

Table 3.4: Refined structural parameters from powder X-ray diffraction data for Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$. Space group $Cmcm$, $a = 18.0862(4)$ Å, $b = 5.5865(2)$ Å, $c = 5.5939(2)$ Å, Volume = 565.20(3) Å$^3$, $Rwp = 0.0758$, $Rp = 0.0574$.

Table 3.5: Refined structural parameters from Powder neutron diffraction data for Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$. Space group $Cmcm$, $a = 18.1455(5)$ Å, $b = 5.5881(2)$ Å, $c = 5.5828(2)$ Å, Volume = 566.10(4) Å$^3$, $Rwp = 0.0876$, $Rp = 0.0922$.

Table 3.6: Variable temperature conductivity of Materials.
Table 4.1: Structural parameters from Rietveld refinement using neutron diffraction data for Li$_2$LaNbTiO$_7$. Space group $\textit{Cmcm}$, $a = 18.2068$ (5)Å, $b = 5.5150(2)$Å, $c = 5.5040(2)$Å, $R_p = 0.0394$.

Table 4.2: Structural parameters from Rietveld refinement using X-ray diffraction data for Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$. Space group $\textit{Cmcm}$, $a = 18.3608(2)$ Å, $b = 5.51830(1)$ Å, $c = 5.5182(1)$ Å, $R_p = 0.888$.

Table 4.3: Variable temperature conductivity of Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.

Table 5.1: Structural parameters from Rietveld refinement using powder neutron diffraction data for Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$. Space group $\textit{I4/mmm}$, $a = 3.8457(1)$ Å, $b = 3.8457(1)$ Å, $c = 26.563(1)$ Å, $R_p = 0.0654$, $R_{wp} = 0.0635$.

Table 5.2: Structural parameters from Rietveld refinement using powder neutron diffraction data for Li$_2$La$_{1.5}$Ti$_2$NbO$_{10}$. Space group $\textit{I4/mmm}$, $a = 3.8629(2)$ Å, $b = 3.8629(2)$ Å, $c = 26.319(2)$ Å, $R_p = 0.0550$, $R_{wp} = 0.0543$.

Table 5.3: Variable temperature conductivity of Materials.

Table 6.1: Refined structural parameters from powder neutron diffraction data for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$. Space group $\textit{P4}_2/\textit{ncm}$, $a = 5.49014(21)$ Å, $c = 26.2456(14)$ Å, $R_p = 0.0997$, $R_{wp} = 0.1197$.

Table 6.2: Refined structural parameters from powder neutron diffraction for Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. Space group $\textit{P4}_2/\textit{ncm}$, $a = 5.49393(19)$ Å, $c = 26.1661(13)$ Å, $R_p = 0.0974$, $R_{wp} = 0.1051$.

Table 6.3: Variable-temperature conductivity of Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

Table 7.1: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$La$_2$Ti$_3$O$_{10}$ in $\textit{I4/mmm}$. $R_p = 0.0578$, $R_{wp} = 0.0764$.

Table 7.2: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$SrLaTaTi$_2$O$_{10}$. Space group $\textit{P4}_2/\textit{ncm}$, $R_p = 0.0896$, $R_{wp} = 0.1237$. 
Table 7.3: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$Sr$_2$Ta$_2$TiO$_{10}$. Space group $P4_2/nmc$, $Rp = 0.0385$, $Rwp = 0.0543$. ..................136

Table 7.4: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$CaLaTaTi$_2$O$_{10}$. Space group $P4_2/nmc$, $Rp = 0.0393$, $Rwp = 0.0522$ ............137

Table 7.5: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$Ca$_2$Ta$_2$TiO$_{10}$ in $P4_2/nmc$. $Rp = 0.0383$, $Rwp = 0.554$ ..........................................................137

Table 7.6: Space group, unit cell parameters, and volumes for all five materials. ...........138

Table 7.7: Variable temperature conductivity of all five materials ........................................142

Table 7.8: Representative R-C values from fits to the Nyquist plots at 200 °C. $R_g$, $R_{gb}$ and $R_{ei}$ indicate the resistances from grain, grain boundary, and electrode-sample interphase. .................................................................................................................142
CHAPTER 1

INTRODUCTION

1. BACKGROUND

The last few decades have seen rapid growth in global energy demand and the lessening of global fuel reserves. The constant utilization of fossil fuel as a source of energy has contributed greatly to the increased greenhouse gases and other environmental problems. To keep global temperatures within a satisfactory range, there is a need to reduce fossil fuel use. This will curb the consistent release of greenhouse gases such as carbon dioxide into the environment. For these purposes, new alternative renewable energy sources such as wind power and solar energy, which are of great economic and social, as well as academic, interest, are needed. This has been the driving force behind various research into new alternative cleaner energy technologies. \(^1\) \(^2\) To utilize such newer technologies effectively, efficient energy storage systems such as batteries, supercapacitors, and fuel cells are needed. These alternative systems for cleaner energy have received remarkable public attention in the past few years. One of the highly convenient and efficient methods of storing energy is in the form of portable chemical energy such as the battery.

A battery provides the portability and mobility of energy storage, with the capacity to convert chemical energy directly into electrical energy with no significant greenhouse emissions. Additionally, the significance of batteries has greatly increased as alternative
energy storage systems because of their use in electric vehicles and other forms of transportation machinery. Additionally, the combination of high energy density and power performance which results from lithium cycling in modern lithium-ion batteries, make them an ideal energy source for portable electronics and other power tools.\textsuperscript{3, 4} Yet, the current commercially available lithium-ion batteries have challenges with cost, safety, possible leakages, spontaneous combustion which is associated with their liquid electrolyte, and service life issues.\textsuperscript{5-8} Hence, obtaining a less expensive, safe, rechargeable battery of high voltage production, high energy capacity, and high cycling capacity is of particular interest.

The replacement of the current electrolytes with solid electrolyte materials could be a solution to the challenges of the current lithium batteries because it can eliminate the existing challenges in these batteries. Owing to their improved safety, solid electrolytes can further achieve higher open-circuit voltages, are resistant to combustion, and finally are leakage-free.\textsuperscript{6, 9, 10} The secondary lithium-ion battery's basic design incorporates an anode and a cathode which are separated and linked together by an electrolyte.\textsuperscript{11} The design comprises a reversible extraction of lithium-ion species from an electrode material that functions as a host matrix for the duration of charge and discharge processes. This lithium extraction process occurs during the migration of lithium ions through the electrolyte material. The electrolyte selectively conducts ions but opposes electron flow through the battery. Such processes are followed by an oxidation-reduction reaction of the host matrix with electron flow across an external circuit. During the charging process, the concentration of lithium-ion intercalation is very high at the anode whereas the cathode is depleted of lithium. However, lithium-ions depart the anode and move through the
electrolyte to the cathode during the discharge state. The associated electrons from the discharge process are then accumulated by a current collector which is utilized by an electric device. The electrochemical oxidation taking place at the cathode can be written as:

\[
\text{Li}_x\text{MO}_2 \rightleftharpoons x \text{Li}^+ + \text{MO}_2 + x e^-
\]

and the anodic reduction involving graphite can be written as:

\[
\text{C}_n + x\text{Li}^+ + xe^- \rightleftharpoons \text{C}_n\text{Li}_x
\]

Lithium-ion batteries usually derive their names from their cathode material, which are always solids,- for instance, the lithium iron phosphate (LiFePO$_4$ - olivines) and lithium cobalt oxide (LiCoO$_2$ - spinel) batteries are made up of LiFePO$_4$ and LiCoO$_2$ cathode materials respectively.$^{11}$ When LiFePO$_4$ is used as a cathode, Li$_x$C$_6$ acts as the anode material, with these electrodes separated by a non-aqueous solution as an electrolyte. During the discharge process, Li$^+$ ions are intercalated in the gaps within the LiFePO$_4$ structure, while charge neutrality is preserved through the reduction of Fe$^{3+}$ to Fe$^{2+}$ ions. The reaction for this process is as follows:

\[
\text{LiFe(II)PO}_4 \rightarrow \text{Fe(III)PO}_4 + \text{Li}^+ + e^-
\]

Similarly, the reverse reaction involving the extraction of lithium ions from the gaps of LiFePO$_4$ structure occurs in the charging process as presented in Figure 1.1.
1.1 BATTERY COMPONENTS

Each lithium-ion battery’s basic design components perform specific functions. The cathode releases Li-ion and collects ions to/from the anode, during the charging/discharging process. The reverse process occurs at the anode during the charging/discharging of the battery. The electrolyte materials help in the transport of ions to/from the two electrodes. All these essential components are made from lithium metal oxide powders, graphite powder, and lithium organic-salt solutions respectively.

1.1.1 ANODE

The battery anode materials are mostly made of lithium-alloys, graphite with copper coating, intermetallic, and in some cases silicon.\textsuperscript{11,12} In principle, using lithium

\begin{figure}
\centering
\includegraphics[width=\textwidth]{lithium-ion-battery-diagram.png}
\caption{Schematic representation of charge/discharge process in a lithium-ion battery.}
\end{figure}
metals as anode materials seems will be ideal. However, this is very challenging due to the many problems such as dendritic growth and erratic cycling behavior (which result in short-circuiting). In the case of carbonaceous anodes such as graphite which are the most widely employed anodic materials, a single lithium-ion can be inserted per each hexagonal gap in the graphite structure. Though carbonaceous compounds are copious and less expensive, their theoretical capacity (372 mAh/g) is poor compared with the charge density of lithium metal (3,862 mAh/g). Due to this, extensive research efforts have been made in the discovery of several novel graphite variations; and several carbon nanotubes have been examined to enhance their capacity. But this comes with a high processing and production cost. Several research works have also been carried out to investigate the capacities of alloys and intermetallics as potential candidates for anodes. Yet, these also yielded poor cycling behavior and show rapid volume changes. \(^{13}\) To overcome these volume dynamics, a few nanocrystalline compounds and alloys with Al, Bi, Mg, Sn among others are still being tested for this application. Moreover, silicon has an exceptionally high capacity of 4,199 mAh/g, which is equivalent to the structure of Si\(_3\)Li\(_{22}\). \(^{13}\) But this capacity is not yet fully understood and the cycling behavior is very poor. \(^{12, 13}\)

1.1.2 CATHODE

The cathode is an essential element of the lithium-ion battery’s design, which consists of a \( \sim 20 \mu \text{m} \) aluminum foil current collector. The current state-of-the-art cathode materials are made up of lithium-metal oxides [such as LiCoO\(_2\), LiMn\(_2\)O\(_4\), and Li(Ni\(_x\)Mn\(_y\)Co\(_z\))O\(_2\)], vanadium oxides, and olivines (such as LiFePO\(_4\)).\(^{12, 14}\) The layered oxide materials containing cobalt and nickel in their structure are the most studied cathode materials for lithium-ion batteries, due to their high stability towards high voltages.\(^{13}\) But
cobalt is limited in availability and toxic in nature, a limitation for its mass production. Although manganese presents a low-cost replacement with a high thermal threshold and exceptional capabilities, it still suffers a few drawbacks that are linked to its cycling behavior. Hence, the combined properties of cobalt, nickel, and manganese are harnessed through making materials that contain mixtures of these elements. Vanadium oxides also demonstrate excellent kinetic behaviors with large capacities. Nevertheless, due to their poor lithium insertion/extraction rates, they tend to be amorphous, thereby limiting the cycling behavior of the cathode. Research works by Goodenough and co-workers discovered materials of the olivines structures such as lithium iron phosphate (LiFePO₄) and related analogs as cathode materials. This discovery is recognized as a breakthrough for rechargeable batteries because of the stable and nontoxic nature of these cathode materials. Moreover, they are less expensive when compared to cobalt, manganese, and nickel-based materials. But they record low conductivity values and moderate capacities which quickly diminish due to cycling. Various approaches of coating these materials have been established to make up for their poor conductivity, but this tends to increase the cost of battery production.

1.1.3 ELECTROLYTE

The central function of the electrolyte is to consistently transport migrating lithium ions across the anode and cathode during the charge and discharge processes. A safe and long-lasting suitable battery electrolyte needs to be stable at existing voltages and high temperatures, have a low melting point and a high boiling point, and must be chemically
and mechanically stable while offering high lithium-ion conductivity. The two main existing electrolyte types are (1) liquid electrolytes and (2) solid electrolytes.

1.1.3.1 LIQUID ELECTROLYTE

Liquid electrolytes are usually Li$^+$ salts in a non-aqueous solvent such as LiBC$_4$O$_8$ (LiBOB), LiPF$_6$, and Li[PF$_6$(C$_2$F$_5$)$_3$]. Generally, the liquid electrolyte is a 1M solution of Li$^+$ salts in solvents such as ethylene carbonate, dimethyl carbonate, and diethyl carbonates. At concentrations higher than 1M, there is significant precipitation of the salts at low temperatures. The key feature is their inflammability; that is, the ideal solvent must have a low boiling point and flashpoint around 30°C. These properties of the electrolyte minimize some common dangers that batteries may pose such as the explosion of the cell and decomposition of electrolytes under high voltages and temperatures. Highly exothermic side reactions and electrolyte decomposition in lithium-ion batteries create a phenomenon known as “thermal runaway.” They also have major limitations such as lithium dissolution. Therefore, choosing an electrolyte frequently requires a balance between flammability and electrochemical performance.

1.1.3.2 SOLID ELECTROLYTE

Examples of solid electrolytes are lithium-ion conductive crystals and ceramic glasses. These electrolytes present numerous improvements which include enhanced safety (no leakages and spills), design flexibility, chemical, and mechanical stability, non-spontaneity, longer life cycle, lighter weight, and resistant to combustion. Batteries with solid-state electrolytes would be capable of shuttling lithium ions efficiently
between electrodes and could offer higher energy density. However, they show very poor low-temperature performance because the mobility of lithium-ion in the solids is greatly reduced at these temperatures. Additionally, they need special deposition and temperature treatment conditions to achieve acceptable behavior. This makes them extremely difficult to handle and expensive to use, although they eliminate separators and the risk of thermal runaway.

The search for solid lithium-ion conductors is ongoing, and several classes of solid-state lithium-ion conductors ranging from solid polymer electrolytes (SPE), inorganic solid electrolytes (ISE), and composite solid electrolytes (CSEs) have been investigated. Recently, a wide variety of ion-conducting solid inorganic oxides of the perovskite and related structures, as well as garnets and lithium silicates, have received enormous considerations and have been examined for this purpose, due to their high lithium-ion conductivity. But they still have several drawbacks too.

The discovery of solid electrolytes with measurable lithium-ion conductivity similar to that of organic liquid electrolytes has proven difficult. Among the inorganic solids examined, only a few solid-state fast lithium ionic conductors such as \( \text{Li}_2\text{La}_3\text{Zr}_2\text{O}_{12} \), \( \text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3 \), \( \text{Li}_4\text{SiO}_4 \), and \( \text{Li}_{10}\text{GeP}_2\text{S}_{12} \), have been discovered. Considering the dependence of their conductivity on temperature, these solids can be classified into (a) high-temperature ionic conductors such as \( \text{Li}_2\text{SO}_4 - \text{Li}_4\text{SiO}_4 \) and \( \text{Li}_{14}\text{ZnGe}_4\text{O}_{16} \) systems, and (b) low-temperature ionic conductors such as \( \text{Li}_{3.6}\text{Ge}_{0.6}\text{V}_{0.4}\text{O}_5 \), \( \text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}\text{(PO}_4)_3 \), and A-site deficient perovskite, \( \text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3 \). All the above lithium conducting solids show measurable ionic conductivities in the magnitude of \( 10^{-3} \)
S cm\(^{-1}\). To date, perovskite-type lithium-containing oxides (ABO\(_3\)) such as Li\(_{3x}\)La\(_{2/3-x}\)TiO\(_3\) (LLTO) and other structurally related compounds are well known as some of the fastest lithium ionic conductors. These perovskites exhibit bulk ionic conductivity, \(\sigma\), as high as \(10^{-3}\) S cm\(^{-1}\) at room temperature. \(^{36,43}\) This conductivity arises from the migration of lithium ions through vacancies in the crystal structure. However, they become electronically conductive within the temperature range of lithium conductivity. \(^{23,32,33,44,45,36,43}\) Researchers continue to examine other promising solid electrolyte candidates of garnets, \(^9,18,19\) lithium silicates, and perovskites. \(^{17,20,22}\)

While it is possible to incorporate Li-ions into a diverse range of solid-state compounds, the conduction pathways that allow the mobility of lithium ions are not available in many lithium-containing compounds.

1.2 DEFECTS IN SOLID MATERIALS

In general, the electrical conduction of metal oxides usually occurs via long-range migration of charge careers such as electrons and ions. While electrons and electron holes are the main electron charge carriers, ionic charge careers may include cations, anions, and external ions which could be impurity ions, dopant ions, and protons. The volume of charge carriers either electrons or ions existing in a metal oxide is directly or indirectly connected to the defect structure of the material.

DEFECTS

Hypothetically, all atoms remain at rest at their lattice sites in perfect crystals, which can be obtained at absolute zero. However, atoms tend to naturally vibrate about
their lattice sites under real conditions. These vibrations are sometimes regarded as defects, and in most cases, a few atoms are certainly misplaced or missing in the crystal structure.

In certain crystals such as high-purity diamond or quartz, the concentration of defect is approximately 1%. On the other hand, several investigations have been made in recent years to determine whether defects should be considered as forming an essential part of the structure rather than just deficiencies in otherwise ideal or highly defective crystal structures.

Most crystals are naturally imperfect due to the existence of defects of certain concentrations. The presence of these defects leads to the reduction of the crystal’s overall free energy. The creation of a single defect such as a vacant cation site in a crystal considerably increases the entropy of the crystal to a greater extent, due to the several available positions which this defect can occupy. Accordingly, there are $\sim 10^{23}$ possible positions for vacancy creations when a crystal holds 1 mol of cations.

On the other hand, the synthesis of most metal oxides leads to various degrees of defects in the material structure. Thus, it is impossible to obtain perfect crystals in every respect from most synthetic routes. Above absolute zero, some defects are always present, and these defects increase the amount of entropy within the crystal. Several classification systems have been projected for crystal defects. Defects can generally be divided into two main categories: stoichiometric defects, where the composition of crystal is retained upon introduction of defects, and non-stoichiometric defects, which result from the change in crystal composition. Also, they are known as intrinsic defects and extrinsic defects, respectively. Furthermore, the sizes and shapes of defects are utilized for classifications such as point defects, which include only one atom or site (vacancies or
interstitials). Occasionally the term extended defects is used to include all other defects which are not point to defects.\textsuperscript{52,53}

1.2.1 INTRINSIC DEFECTS

Schottky and Frenkel are two widely known types of intrinsic defects found in halide and oxide compounds. These types of defects may arise in isolation owing to the increased entropy of the compounds. As temperature rises, the thermal vibrations of ions within a crystal increase about their lattice positions. In cases where the vibrations of an ion are large enough, it may hop out of its lattice position resulting in the creation of a point defect. At much higher temperatures there is a higher possibility for the lattice site to be vacant. These are thermodynamic defects as the concentration of defects is a function of temperature. In oxide ionic materials, the Schottky defect, which is a stoichiometric defect consists of a 1:1 pair of anion vacant site and cation vacant site as presented in Figure 1.2.1a for MX type solids such as NaCl. To compensate for the vacant sites, two additional atoms at the crystal’s surface for each Schottky defect are needed and there must be equivalent numbers of anion and cation vacancies to maintain electroneutrality. Vacancies may also be randomly distributed through the crystal or may associate in pairs or larger clusters. For compounds with $MX_2$ type structure, the defect will involve one $M^{2+}$ cation vacant site and two anion vacant sites.

A Frenkel defect involves the displacement or movement of an atom or ion from its lattice site into an interstitial position that is normally empty as illustrated in Figure 1.2.1b. Frenkel defects may occur on either cation or anion sublattice. In general, defects of this type at the cation site occur more frequently than those of anions because the size
of cations is much smaller. Thus, these ions can easily be accommodated at interstitial sites with the materials. The direct impact of Frenkel defects is that a crystalline solid tend to conduct electricity to some extent.\textsuperscript{54, 55}

\textbf{Figure 1.2.1:} Representation of intrinsic defects in compound composition type MX. a) Schottky defect b) Frenkel defect.

1.2.2 EXTRINSIC DEFECTS

Extrinsic defects are introduced into solid materials when cationic dopant impurities with unequal valences replace the cations of the solid. Real crystals usually contain both intrinsic and extrinsic defects in their structure. However, the dominating defect type solely depends on parameters such as temperature and the doping or non-stoichiometry concentration levels. Many solid compounds are susceptible to aliovalent substitution, where a metal atom or ion can be replaced by another element with a similar size and bonding requirements. When the oxidation state of the element ion is different from the ion it is replacing, the charge balance mechanism needs to be preserved to retain
electroneutrality. This approach results in vacancies in the cation, anion or interstitial

cation, and anion sites.\textsuperscript{53-56}

1.3 CONDUCTIVITY

Crucial to the success story of our research is the capacity to impact the ionic

conductivity properties of the layered materials under investigation. The essential material

properties in our view are directly dependent on the ease of mobility of charge-carrying

species such as ions through the spaces within the solid materials. Thus, it is vital to control

parameters such as lithium-ion concentration, and key defect concentrations within the

crystal structures. The following section presents a summary of the theory of conductivity,

which includes ionic and electronic conductivities.

1.3.1 ELECTRICAL CONDUCTIVITY

The partial electrical conductivity, $\sigma_j$, of charge carrier species $j$ can be expressed

using the equation:

$$\sigma_j = \mu_j \cdot n_j \cdot e_j$$  \hspace{1cm} (1.3)

where $\mu$ represents the mobility of charge carriers, $n$ is the concentration of charge carriers,

and $e$ is the charge of the carrier species (e.g. +1 for Li$^+$). Then, the total sum of

conductivities $\sigma_i$ in a solid of various carrier species is given by:

$$\sigma_{tot} = \Sigma \sigma_i$$  \hspace{1cm} (1.4)
where charge carriers in our case are lithium ions. These may also be electrons, holes and in some cases oxide ions for oxide conducting materials. In materials where all these charge carriers are present, equation 1.4 becomes:

$$\sigma_{\text{tot}} = \sigma_i + \sigma_j + \sigma_k$$

(1.5)

where ionic conductivity, electronic conductivity, and holes are represented by \(\sigma_i\), \(\sigma_j\), and \(\sigma_k\) respectively. The electrons and ions are the charged species in all forms of oxide materials, which may have contributions arising from various transport mechanisms. Some of these significant transport processes contribute to electronic conductivity which arises from doping with an electron donor, also known as \(n\)-type conductivity, or from electron holes, which is termed \(p\)-type conductivity. However, for a purely ionic conductor (lithium-ion conductor) for battery electrolyte applications, it is required that only contributions from ions should be present.

The ionic conductivity, \(\sigma_{\text{ion}}\), and electronic conductivity, \(\sigma_{\text{ele}}\) in equation 1.5 can further be expressed using their transport or transference numbers:

$$\sigma = \sigma (t_{\text{ion}} + t_{\text{ele}}) = \sigma (t_{\text{cat}} + t_{\text{an}} + t_n + t_p)$$

(1.6)

where the conductivities of cations, anions, electrons, and electron holes are represented by \(\sigma_{\text{cat}}\), \(\sigma_{\text{an}}\), \(\sigma_n\), and \(\sigma_p\) respectively. The sum of these transport or transference numbers for all charged species (ions and electrons) is equal to one.

$$t_{\text{ion}} + t_{\text{ele}} = t_{\text{cat}} + t_{\text{an}} + t_n + t_p$$

(1.7)
The transference or transport number characterizes the comparative contributions of charge carriers (ionic, \( \sigma_i \)) to the total conductivity of the solid as seen below:

\[
I_{\text{ion}} = \frac{\sigma_i}{\sigma_{\text{tot}}} \tag{1.8}
\]

Similarly, one can also define transference numbers for electrons and holes.

### 1.3.2 ELECTRONIC CONDUCTIVITY

The electrical conductivity properties in most oxide materials are dominated by electronic contributions as compared to ionic contributions, even in solids with fewer concentrations of electron charge carriers than ionic charge carriers. Typically, only one type of charge carrier dominates in a solid oxide material at a specific temperature. Band theory can be used to illustrate and highlight the disparity between the electronic structures of metals, semiconductors, and other types of solids. As illustrated in Figure 1.3.1, the valence band (highest occupied band) of a metallic material overlaps with the conduction band. Metallic materials exhibit higher magnitudes of conductivity because electrons in singly occupied states close to the Fermi level are very mobile.
Figure 1.3.1: Band structure of a metal

On the other hand, the valence band of insulating material is filled and separated from the next empty band by a very large bandgap. The conductivity in insulators is almost negligible because only a handful of electrons have sufficient thermal energy to overcome the wide energy gap between the valence band and the conduction band. Figure 1.3.2 describes the band structure of a typical insulator.\textsuperscript{52, 55-57}

Figure 1.3.2: Band structure of an insulator
The band structure of semiconductors closely resembles that of insulators (Figure 1.3.3). Unlike insulators, the bandgap between the valence and conduction bands is within the range of 0.5 to 3.0 eV. This allows for the easier promotion of electrons from the valence band into the conduction band as compared to insulators.

When a potential is applied to a semiconductor, the negatively charged species drift towards a positive electrode while leaving behind vacant holes that are considered positive holes. These holes are mobile in the presence of electrons, thereby creating fresh holes at their original positions. These positive holes move in the direction opposite to electron movement within the semiconducting material.

![Band structure of a semiconductor](image)

**Figure 1.3.3:** Band structure of a semiconductor.

There are two broad classifications of semiconductors: intrinsic and extrinsic semiconductors. Intrinsic semiconductors are pure materials, whose electron count in the conduction band is dependent on the temperature and the magnitude of their bandgap. The band structure of such semiconductors is illustrated in Figure 1.3.4 below:
Figure 1.3.4: Positive and negative charge carriers in semiconducting solids.

For extrinsic semiconductors, the conductive properties are regulated through the addition of dopants. For instance, semiconductors such as pure silicon which are originally intrinsic can undergo a transformation into extrinsic semiconductors by doping with Group III or V elements from the periodic table. Doping silicon with a small concentration of gallium (~1ppm) results in the formation of discrete levels right above the valence band, as gallium has one electron short in its valence as compared to silicon. This level is known as the acceptor level due to its capability of accepting electrons. Owing to the proximity of the energy bandgap between this acceptor level and the valence band, electrons within the valence band have enough thermal energy to hop into the acceptor levels. However, electrons in the acceptor level cannot contribute to conduction in the semiconductor, as the acceptor levels are discrete due to the low concentration of gallium atoms. Moreover, the positive holes which are left behind in the valence band are responsible for the conductivity of materials of this type as presented in Figure 1.3.5a.
Figure 1.3.5: Types of semiconductors. a) p-type semi conductivity in gallium-doped silicon. b) n-type semi conductivity in arsenic-doped silicon.

Doping silicon with a little concentration of arsenic (~ 1ppm) on the hand leads to the formation of discrete levels about 0.1 eV below the conduction band. Here, the extra electron of arsenic occupies these discrete levels as seen in Figure 1.3.5b. These levels unlike the acceptor levels in p-type semiconductors can directly contribute to conduction. The electrons have sufficient energy to hop into the conduction band and hence act as donor levels in the semiconducting materials. Materials of this kind are known as n-type semiconductors.

At ambient temperatures, the extrinsic charge carrier concentrations are much higher than intrinsic carrier concentrations. So, the conductivity is regulated by the extrinsic carrier concentration within materials. However, when temperatures are sufficiently high, a conversion to an intrinsic behavior would be observed as the intrinsic carrier concentrations are greater at these temperatures. Figure 1.3.6 shows the temperature dependence of conductivity and carrier concentrations for extrinsic semiconductors at lower temperatures and intrinsic semiconductors at higher temperatures.
1.3.3 IONIC CONDUCTIVITY

The presence of defects in ionic solids facilitates and enhances the mobility of ions under an applied electric field. The migrations of defects, vacancies, and ions in the interstice sites of ionic solids result in ionic conduction. The extent of conductivity in these solids can be directly associated with the concentration of defects existing within the crystal. For ionic conduction through vacancies within a material, two strategies can be used in vacancy creation. Both intrinsic and extrinsic vacancies can be created by heating or doping in order to improve the ionic conductivity. The dependence of ionic conductivity of temperature follows the Arrhenius equation presented below:

\[ \sigma = A \exp \left( \frac{-E_a}{kT} \right) \]  

(1.9)

where is the ionic conductivity, Ea, k, T, and A represents the activation energy, the Boltzmann constant, the absolute temperature, and the pre-exponential factor respectively.
MECHANISM FOR IONIC CONDUCTIONS

The conduction mechanism principles outlined in this section are valid for most ionic oxides such as lithium and sodium-containing solids (Li⁺ and Na⁺) as well as oxide ion conductors. The mechanism via which lithium-ion vacancies migrate within the lattice is depicted in Figure 1.3.7. A lithium-ion hops from an occupied lattice site to a neighboring vacant site through a thermally activated process. As the lithium-ion jumps, it passes through space within the lattice with a potential energy barrier. The experimental result suggests the availability of open spaces and available unoccupied lattice sites for lithium ions to fill is one of the crucial parameters in enhancing lithium conductivity in oxide materials. This is similar for oxide ion conductors too. This directly impacts the nature of the activation energy barrier, $E_a$, needed for the hopping motion of ions to occur.

![Figure 1.3.7: Ion hopping mechanism in ionic solids.](image)

The equation for the direct dependence of ion mobility on this parameter can be expressed as:

$$\mu = \mu_o \exp \left( \frac{-E_a}{kT} \right)$$

(1.10)
where $\mu_0$, $E_a$ and $T$ represent the pre-exponential factors, activation energy, and the temperature in degrees Kelvin respectively. The pre-exponential factor comprises factors such as the attempt frequency, the hopping distance, the number of vacant neighboring sites as well as other geometric and correlation effects. The temperature dependence of conductivity can also be expressed using the modified Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} \exp \left( \frac{-E_a}{kT} \right)$$  \hfill (1.11)

From this modified expression, the $E_a$ can be obtained by plotting $\ln (\sigma.T)$ as a function of $1/T$ and extracting the slope. Also, the intercept of the line on $\ln (\sigma.T)$ relates to the pre-exponential term, $\sigma_0$.

Structural geometrical considerations have also been used to facilitate the mobility of ions of any kind in an ionic conductor. Since the ionic conduction can be regulated by the motion of ions throughout the lattice available spaces, a larger space through which the ions can move will increase its mobility. For instance, Kilner and Brook suggested the concept of "free volume", in particular cases, through the use of larger cations to induce close-packed ions such as oxide anions to move apart.\textsuperscript{59} Also, the direct correlation between material chemical composition has been reported to greatly impact the lithium-ion conductivity of some perovskite oxide materials.\textsuperscript{42, 58, 61}

1.4 CHEMICAL DIFFUSION

This section covers the relationship between the chemical diffusion coefficient and the conductivity of charge carriers. Chemical diffusion is a process that involves the transport of coupled species in a solid. Generally, the flux density of species usually in
particles per square centimeter seconds in solids are expressed using Fick’s law of
diffusion:62,63

\[ j_j = -D_j \frac{\partial c_j}{\partial x} \]  (1.12)

where \( D_j, c_j \) and \( x \) represent the chemical diffusion coefficient, concentration of species \( j \)
and direction of the concentration gradient respectively. The diffusion coefficient characterizes the weighted average of all chemical diffusion coefficients of every species contributing to the overall observed transport process within the solid. For instance, when a solid is a mixed ionic and electronic conductor, where the whole conduction process involves contributions from ionic and electronic charge carriers, the chemical diffusion coefficient can be expressed using the equation:

\[ D = t_i D_i + t_e D_e \]  (1.13)

where \( D \) represents the overall chemical diffusion coefficient, \( t_i \) and \( t_e \) are the ionic and electronic transport numbers and \( D_i \) and \( D_e \) are the diffusion coefficients of ions and the electronic charge carrier species respectively. In most occurrences, the mobility of the electronic charge carriers is much greater than that of ions such that, \( D_e \gg D_i \) is a valid approximation. Moreover, when the conductivity is predominantly electronic (\( t_e \sim 1 \)) under specified conditions such as high temperature, equation 1.13 becomes:

\[ D = D_i \]  (1.14)

This is an indication that the diffusion coefficient of the ionic species in a material can be provided from the measurement of the chemical diffusion coefficient under the conditions specified. The mobility of ionic species is related to the diffusion coefficient by:

\[ \mu_j = \frac{z_j e D_j}{kT} \]  (1.15)
which is a modified form of the Nernst-Einstein relation, where \( z, e, D, k, \) and \( T \) represent the number of nearest-neighbor sites, the charge of the carrier species, the diffusion coefficient, the Boltzmann constant, and the temperature in degree Kelvin respectively. Through substitution of equation 1.15 into equation 1.3, the conductivity of species \( j \) can be estimated by:

\[
\sigma_j = \frac{D_j z^2 j e^2 c_j}{kT} \tag{1.16}
\]

1.5 EXPERIMENTAL TECHNIQUES

Material chemistry focuses on the study of the synthesis, structure determination, chemical, and physical properties as well as the significant applications of solid materials non-molecular solids. Non-molecular solids are compounds that contain networks of atoms connected through the material, rather than having individual molecules. Generally, the structure of solid crystals can be directly linked to their overall properties. Hence, research investigations in solid-state chemistry are geared toward the acquisition of detailed knowledge on major parameters such as how the chemistry impacts the structure of a material and how this structure can be connected to the measured physical properties.

A typical example is the study of the structure-property relationship in perovskite oxides and their related materials such as the layered perovskites of the Ruddlesden-Popper type structure. Extensive studies have been conducted into the ion-exchange,\(^{64, 65}\) photocatalysis,\(^{66}\) magneto-resistance,\(^{67, 68}\) and susceptibility to intercalation,\(^{69}\) and more recently carbon dioxide (CO\(_2\)) capture,\(^{70}\) and ionic conductivity of these materials.\(^{65, 71}\) The
structural properties of materials in this class can be tuned through simple elemental substitutions at the A or B site and creation of defects at specific sites within their crystals.

1.6 MATERIAL SYNTHESIS

All materials presented in this work were synthesized using conventional solid-state methods, which involve mixing stoichiometric amounts of suitable reagents, pelletizing, and heating at high temperatures. This mixing and pelletizing approach ensure a homogeneous mixture of desired reaction constituents is obtained. In this work, high purity binary oxides or carbonates with suitable cations were utilized. Reaction mixtures were then sintered in alumina boats at suitable temperatures under appropriate reaction conditions. Reaction conditions can be oxidizing (in the air or flowing oxygen gas) or reducing (H\textsubscript{2}(g) / N\textsubscript{2}(g) mixture) or an inert atmosphere (in argon) or nitrogen). The solid-state reaction occurs at the interfaces between reactant grains through an ion diffusion mechanism at a high temperature, which is extremely slow. Thus, these reactions solely rest on ions' diffusion rate towards the grain boundaries. These ions require adequate energy to drift towards these boundaries. For such synthesis in general, no solvents or solutions are needed. The reactions are driven by high temperatures and longer reaction times. However, in cases such as co-precipitation, sol-gel, and plasma approaches, some steps of the synthesis involve dissolution in solvents, followed by decomposition of precursor compounds at high temperatures after drying. The grains of the desired product increase in size as the reaction progresses. Recurrent grinding between sequential heat treatments is required to form more products via the creations of new interfaces between reactant particles. \textsuperscript{72}
1.6.1 CHARACTERIZATION TECHNIQUE OF SOLID-STATE MATERIALS

1.6.1.1 POWDER DIFFRACTION

X-ray and neutron powder diffraction is the most extensively utilized method for the identification of the accurate regular 3D arrangement of the atoms, which includes atomic positions, interatomic distances, and bond angles. These techniques were employed in the structural elucidation of materials presented in this work. Powder X-ray diffraction (XRD) is by far the most significant method for identifying crystalline materials. It may be utilized in various ways in the study of solid solutions too. For instance, it is employed as a simple fingerprint detections procedure in the determination of specific phases present in crystalline solids without necessarily investigating the details of their structures. It is a helpful technique for the accurate determination of the unit cell dimensions, which typically may undergo some contractions or expansions as the composition constituent change. Usually, the material lattice undergoes expansions when smaller ions are substituted by larger ions and vice versa. The location of powder diffraction peaks of crystalline materials is dependent on the unit cell parameters. Thus, the entire diffraction pattern shifts towards lower 2θ values with increasing unit cell parameters, though all the diffraction lines may not necessarily move by the same magnitude in non-cubic crystal systems if the expansion is not isotropic. Given the angle dependence of the peak patterns and intensities in XRD, the peaks at a high 2θ angle are generally less pronounced. The phase purity of materials is then determined through a comparison of collected peak patterns with those of a database using a search and match process in a qualitative phase analysis. The crystal system and material phase are then confirmed using Rietveld refinement profile analysis by different computer programs.
From these analyses, one can gain detailed crystallographic data such as the site occupancies of atoms and vacancies and interstitial locations within the material.

1.6.1.2 BRAGG EQUATION

When a monochromatic X-ray beam strikes individual electrons, the beams are scattered homogeneously in every direction. Hence, the regular arrangements of atoms act as scattering points in diffracting X-rays within a crystal. These diffractions can occur constructively or destructively contingent on the wave overlap patterns with each other. When the waves are in phase with one another, constructive interference occurs whereas destructive interference involves out-of-phase movements of diffracted waves. Powder diffraction is better understood through the considerations of the Bragg equation.

A segment of a crystal with an array of atoms positioned on a set of imaginary parallel planes and spaced out by interplanar distance $d$ is presented in Figure 1.4.1 These crystallographic planes are categorized by the triplet indices known as Miller indices $(hkl)$. Several different sets of planes may run in different directions in a crystal, due to their location relative to the axes of the unit cell. As seen in Figure 1.4.1, when radiation of wavelength, $\lambda$ strikes these crystallographic planes at an angle $\theta$, the reflected rays from the plane below travel a lengthier distance than rays reflected from the planes above. The distance covered by these reflected radiations is equivalent to the combination of the distance $AX + BX$, which is expressed as:

$$AX + BX = 2d \sin\theta$$

(1.17)

For constructive interference to transpire, this additional distance should be equivalent to an integral sum of wavelengths,
\[ n \lambda = AX + BX \]  

(1.18)

Hence,

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

(1.19)

This equation, also known as Bragg’s law, highlights the important conditions to meet if diffraction must occur. The \( n \) in this equation represents the order of reflection. \(^{52,72}\)

---

**Figure 1.4.1:** A graphical representation of Bragg’s law.

---

1.6.1.3 NEUTRON POWDER DIFFRACTION

Neutron powder diffraction is a very important and expensive technique that requires intense neutron flux, that can be generated by a nuclear reactor or a spallation source. Thus, only a few laboratories have neutron facilities, and most experiments are carried out in central and national laboratories. This technique requires sufficiently large volumes of the sample as neutron interaction with the sample is much weaker than that of X-rays. Also, neutron sources are usually of low intensities. Unlike X-ray which interacts
with electron clouds and scatters more strongly for heavier atoms, neutron interacts with the nuclei and hence diffracted strongly by both lighter and heavier atoms and can easily discriminate between various isotopes. This allows for the accurate determination of site occupancies and atomic positions of lighter atoms such as lithium via neutron diffraction. The scattering power of neutrons does not decrease significantly as compared to that of X-rays which decreases with increasing $2\theta$ angles. So, neutron powder diffraction provides more information at high angles and can also be used to determine reliable temperature factors.

1.6.1.4 ELECTRICAL CONDUCTIVITY CHARACTERIZATIONS

The ionic conductivity measurements were carried out utilizing AC impedance spectroscopy. A brief background of this technique is provided in the section below:

1.6.1.5 AC IMPEDANCE SPECTROSCOPY

Evaluation of electrical conductivity is usually carried out via the measurement of the electrical resistance of a sample under an applied voltage. However, the electrical response changes with whether the resistance is ionic or electronic in nature. It is a characteristic of the internal dynamics of the material. Figure 1.5.1 demonstrates the behavior of electronic conductors, ionic or mixed conductors under an applied potential. In electronic conductors, the current reaches a constant value almost immediately when a constant potential is applied. Then, the potential and the current will remain constant over time as presented in Figure 1.5.1. In ionic conductors, on the other hand, mobile ionic species reorganize internally to counter the applied external potential. Hence, when a
potential is applied, lithium-ions will migrate towards negative electrodes and any existing vacancy in the opposite direction, respectively. Consequently, this results in internal polarizations that solid material experiences from the motion of opposing charged species towards opposite electrodes. As a result of such polarization, the mobility of charged particles drops with time, as electrodes block the ionic current. In mixed conductors, on the other hand, the current theoretically decreases to a value that is a function of the magnitude of the electronic conduction. Hence, in principle, ac impedance spectroscopy can be used to estimate the value of the electronic conductivity in a mixed ionic/electronic conductor. However, in practice, this method is very challenging due to the internal seclusion of ions, among other factors. 73

Subsequently, 2-probe direct current (DC) measurements of nature explained above are not used to determine ionic conductivity in solids. Instead, the method of choice for this purpose is AC impedance spectroscopy. 74 Impedance is the alternating current analog to resistance for direct current.

In a DC measurement, the resistance is expressed as:

\[ R = \frac{V}{I} \]  

(1.20)

AC impedance is determined in a related manner. The technique is centered on applying a small potential, \( v(t) \), to a sample. The signal follows a sinusoidal relationship:

\[ v(t) = V_m \sin(\omega t) \]  

(1.21)

where \( V_m \) represents the amplitude voltage and \( \omega \) is the angular frequency in Hz. The resultant steady-state current of the system is calculated as a function of the signal over a range of frequencies.

\[ i(t) = I_m \sin(\omega t + \Phi) \]  

(1.22)
where $\Phi$ is the phase shift. Thus, the impedance is then described as:

$$Z(\omega) = \frac{V(t)}{I(t)}$$  \hfill (1.23)

which may be rewritten in relation to its real and imaginary components

$$Z = Z' + iZ''$$  \hfill (1.24)

By plotting the imaginary ($Z''$) vs. real ($Z'$) parts in the complex impedance plane as a function of angular frequency, essential information about the resistance and capacitance of the sample and the basis of all contributions to that resistance may be acquired. Towards understanding this procedure, it is necessary to recognize the various contributions towards the overall resistance in an AC experiment.

In a polycrystalline material, the conduction pathways can always be related to the resistance and capacitance of the material. Therefore, the bulk of the material can be modeled using resistance-capacitance (R-C) circuit units. However, charge transport occurs within internal grains, and across boundaries between grains. This conduction across these boundaries can also be explained using a resistance-capacitance (R-C) model. Additionally, the charge transfer across electrodes can also be seen in a similar manner. These RC-circuit parts are usually regarded as a series circuit, describing the ultimate conduction process within the material. Each component contributes its impedance as illustrated in Figure 1.5.2. The electrical pathway can be modeled with resistance-capacitance units as represented in Figure 1.5.2.
Figure 1.5.1: Variation of current as a function of time in electronic, ionic, and mixed ionic/electronic conductors.

Figure 1.5.2: Resistance-capacitance circuit units describing electrical contributions from different components of a material.

In principle, the product of $R$ and $C$ is known as the time constant which is distinct for all components of the conduction process. Thus, each R-C circuit unit can be expressed using:

$$Z = \frac{1}{\left(\frac{1}{R} + j(2\pi fC)\right)}$$  \hspace{1cm} (1.25)
Where R represents the resistance in ohms, f and C are the frequency in Hz and the capacitance in Farads. When equation 1.25 is multiplied with the complex conjugate of its denominator, it is possible to separate the real and imaginary components as:

\[
Z' = \frac{\frac{1}{R}}{(\frac{1}{R})^2 + j(2\pi f C)^2}
\]

(1.26)

\[
Z'' = \frac{2\pi f C}{(\frac{1}{R})^2 + j(2\pi f C)^2}
\]

(1.27)

These reduce to the equation of a circle with a center at \((\frac{R}{2}, 0)\) and radius \((\frac{R}{2})\):

\[
(Z'')^2 + (Z' - \frac{R}{2})^2 = (\frac{R}{2})^2
\]

(1.28)

When the time constants linked with the individual contributions are significantly different, three different arcs are expected to form in a plot of \(Z''\) vs. \(Z'\), which characteristically describes the conduction process. This hardly occurs in real experimental setups as presented in Figure 1.5.3, which includes arcs corresponding to the bulk(grain) and grain boundary and in some cases electrode effects combined to form a single depressing arc. Experimentally it is challenging to separate the arc corresponding to bulk from the grain boundary conduction processes. Therefore, the total conductivity is commonly reported for the material as the combination of all contributions. This situation was commonly encountered during this research work.
Thus, the conductivity values reported in later sections of this work were derived from the sum of contributions arising from the bulk and grain boundary resistivities. It should be noted that separations of these individual conductivity contributions can be achieved using computer programs such as Zview, EC-lab, and EIS analyzers among others. These programs were utilized in highlighting various conductivity contributions that arise in the different materials studied in this work as presented in later chapters. Though the bulk conductivities are an inherent material property, the grain boundary characterizes a parameter that may be improved by suitable control of the microstructure of the material.

Scanning electron microscopy (SEM) gives detailed information on the micro-structures, particle sizes, and shapes over a broad range of magnifications. SEM also has a supplementary feature that allows elemental analysis, and the mapping of elemental distributions is a specific solid material. This technique is known as energy dispersive X-ray detection (EDX). When high-energy electrons impinge on a compound, X-rays are generated. These X-ray radiations are characteristic of the element producing it. EDX

**Figure 1.5.3:** Representative Impedance plot of a polycrystalline material.
analyzes and determines elements by examining either the wavelength or the energy of X-rays emitted.

1.7 PEROVSKITES OXIDES

1.7.1 PEROVSKITE STRUCTURE

Perovskites and their related materials are an important class of inorganic solids that have been widely studied due to the variety of interesting physical properties they exhibit. Perovskite materials have great flexibility in composition, incorporating many members from the periodic table which can be exploited or modified to enhance their physical properties. These compounds are of the general form ABX$_3$ and can assume a wide variety of related structures depending on the relative sizes of cations at the A and B-site, as well as the type of chemical bonding based on the BX$_6$ octahedra network. Cations at the A-site are usually rare-earth or alkaline earth elements residing within the interstitial spaces between BX$_6$ while B is a transition metal or metal cation from the $p$ block (mostly group 13 elements). The metals are coordinated by anions X, such as oxides, carbides, nitrides, or halides where the oxides and fluorides are the most found. The basic framework of perovskite materials is made up of a three-dimensional array of units interconnected through the corners of BX$_6$ octahedra, as seen in Figure 1.6.1.

While some perovskite compounds have an ideal cubic structure, several others and perovskite-related materials have slightly distorted lower symmetry variations, because of the difference in ionic radii of cations occupying the A and B-sites. This results in the observed Jahn-Teller distortions and a deviation from the ideal composition and structure.
These distortions in most cases can be assigned to several other factors existing within these compounds.

\[ r_A + r_X = \sqrt{2}(r_B + r_X) \]  

\[ t = \frac{r_A+r_X}{\sqrt{2}(r_B+r_X)} \]
Again, \( r_A, r_B, \) and \( r_X \) represent the radii of the \( A \) and \( B \) cations and \( X \) anions, respectively. The tolerance factor for an ideal cubic perovskite is one (1), where \( A \)-site cations are larger than the corresponding \( B \)-site cations. When the \( A:B \) ratio becomes larger than that of the ideal cubic perovskite, the tolerance factor becomes less than one (1). This leads to an elongation of \( B - X \) bonds while placing \( A - X \) bonds under tension.

Consequently, lower magnitudes of \( t \) lower the overall symmetry of the crystal structure. Also, when \( t \) is greater than one due to the presence of a large \( A \) cation or a correspondingly smaller \( B \)-site cation, \( B \) dislodges from the center of the \( BX_6 \) octahedra to improve the bonding between \( B \) and \( X \). A wide variety of other complex metal oxide structures contain the perovskite unit. An example is the layered perovskite oxides of the Ruddlesden-Popper structure, which features \( BO_6 \) inter-stacks units separated by rock salt type components, to form a series of \( A_{n-1}A'B_nO_{3n+1} \) structures.

This dissertation focuses on the design, synthesis, characterization, and physical property exploitations of layered perovskites of this structural type towards the enhancement of ionic conduction in these solids.

1.7.2 LAYERED PEROVSKITE OXIDES: RUDDLESDEN-POPPER STRUCTURE

Layered perovskites constitute two-dimensional (2D) blocks of the perovskite \((ABO_3)\) structural units, separated by species within the interlayer spaces. Materials of the Dion-Jacobson (DJ), \( A'\underset{n-1}{A}B_nO_{3n+1} \), Ruddlesden-Popper (RP), \( A_Z\underset{n-1}{A}B_nO_{3n+1} \) and Aurivillius (AV), \((Bi_2O_2)\underset{n-1}{A}B_nO_{3n+1}\) structural types are well studied layered perovskites, where \( A/A' \) represent an alkali metal, alkaline earth metal or a lanthanide metal, and \( B \) is usually a transition metal.\(^{51}\)
Ruddlesden-Popper (RP) phases are two-dimensional (2D) layered perovskite materials with general formula $A_2'A_{n-1}B_nO_{3n+1}$. They are defined by layers of AO oxide intercalated by variable ABO$_3$ perovskite blocks characterized by $n = 1, 2, 3, \ldots \infty$, stacked together in alternating order in the $c$-direction. In these materials, cation $A$ represents an alkali, alkaline-earth, or rare earth metal, and the $B$-site is occupied by a transition metal element. It is feasible to mix two cation types at either the A or B-sites, which can be represented as AA’ or BB’. The A-site cations occupy nine and twelve coordinate interstitial sites, whereas the B-site cations occupy octahedral positions (coordination number = 6) as presented in Figure 1.7.1.

![Figure 1.7.1: Ruddlesden-Popper materials showing different layers.](image)

The swing from 3D to 2D through corner-sharing BO$_6$ octahedra in the RP compounds plays a vital role in their observed electrical conductivity properties. For instance, the perovskite SrRuO$_3$ shows a metallic conductivity behavior, while Sr$_2$RuO$_4$ of the RP type structure shows superconductivity at relatively lower temperatures. Octahedral rotations in perovskite-based materials are usually the result of several different
factors such as preferential coordination of the A-site cation or pressure/epitaxial strain associated with the compound. Similarly, the octahedral layer in RP compounds has at least two associated distortion modes: a rotational and a tilting mode. Each of these modes eventually condenses into various space group symmetries and different structural properties.

RP solids have an exceptionally wide range of potential applications because they display diverse interesting properties such as catalysis, ion-exchange reactions, magneto-resistance, superconductivity, optical properties, carbon dioxide (CO₂) capture, and intercalation. Given the large available spaces separating the perovskite stacks and various structural distortions, it is rational to speculate that these inter-layer gaps could be excellent channels for the transport of ions. If different ions could be inserted into these layers through synthesis, variable material properties could be attained. However, only a handful of lithium-based Ruddlesden-Popper materials have been reported over the last few years, with Li-ions residing in inter-stack spaces. Transport processes and ionic mobility in these materials have further been reported to take place through the lithium layers.

1.8 RUDDLESDEN-POPPER OXIDES AS POTENTIAL SOLID ELECTROLYTE

The development of new electrochemical energy conversion and storage devices such as supercapacitors and rechargeable lithium batteries is of prime significance to mitigate the energy and environmental challenges. The commercial rechargeable lithium-ion batteries that operate based on lithium cycling have transformed the portable
electronics industry. Their high energy density has also attracted much attention for potential application in large scale power grids and electric vehicles. However, the rechargeable lithium batteries may not be able to satisfy future demands in large-scale energy storage applications due to risks of leakage and combustion resulting from the flammable nature of their liquid organic electrolytes. Safety issues, particularly relating to flammability, have hampered the development of commercial liquid batteries. Additionally, the tendency to form lithium dendrites during repeated charge/discharge cycles has hindered the commercial use of lithium metal as an electrode in rechargeable batteries, even though lithium metal possesses very high theoretical specific capacity (3860 mAh g⁻¹), low mass, and the least negative electrochemical potential (-3.04 V vs. SHE).

One avenue for enhancing the energy and power densities of lithium-ion batteries while improving their safety is the development of all-solid-state lithium-ion batteries consisting of solid electrolytes and electrodes. Advances in all-solid-state batteries require the development of solid electrolytes (section 1.3.2) which can help address the safety concerns and achieve higher open-circuit voltage, which in turn will facilitate the use of high voltage cathode materials and metal anodes for long term stability.

Ruddlesden-Popper oxides can be good lithium-ion conductors for solid electrolyte applications. However, their lithium transport properties have received little attention despite their interesting structural properties and distortions that can provide useful pathways for lithium mobility. They feature large gaps in their structure that can be explored to achieve high Li-ion conductivity. Yet only a small number of Ruddlesden-Popper oxides containing lithium have been reported where the Li-
ions reside at those spaces. Among the bilayer, \( n = 2 \), Ruddlesden-Popper oxides, the electrical properties of \( \text{Li}_2\text{SrTa}_2\text{O}_7 \) have been studied, showing lithium-ion conductivity of \( \sim 10^{-7} - 10^{-5} \text{ S cm}^{-1} \) in the temperature range 250 – 500 °C.\(^{43}\)

While the ionic conductivity of \( \text{Li}_2\text{SrTa}_2\text{O}_7 \) is not significant, it demonstrates the feasibility of lithium conduction in Ruddlesden–Popper phases. This is reminiscent of the initial stages of research on some other ionic conductors, such as garnet oxides, where the first materials showed low lithium ion mobility,\(^{21}\) but further modifications led to the synthesis of highly conductive materials.\(^{18-20,31}\) There has also been a study in the same material series, where the conductivity of poly(ethylene oxide) composite with Ruddlesden-Popper oxides has been investigated, showing conductivity of \( \sim 10^{-6} \text{ S cm}^{-1} \) at 80 °C.\(^{35}\) Other studies involving \( \text{Li}_2\text{SrNb}_2\text{O}_7 \) (2.10 \( \times \) \( 10^{-6} \text{ S cm}^{-1} \) at 200 °C),\(^{90}\) \( \text{Li}_2\text{Sr}_{1.5}\text{Nb}_3\text{O}_{10} \) (4.90 \( \times \) \( 10^{-6} \text{ S cm}^{-1} \) at 280 °C),\(^{91}\) and \( \text{Li}_2\text{Sr}_{1.5}\text{Nb}_{2.885}\text{Fe}_{0.117}\text{O}_{10} \) (9.60 \( \times \) \( 10^{-5} \text{ S cm}^{-1} \) at 390 °C)\(^{65}\) show similar conductivity patterns across all temperatures as reported for \( \text{Li}_2\text{SrTa}_2\text{O}_7 \). These Li-ion conductivities are lower than those of fast lithium-ion conductors such as garnets (\( \sim 10^{-4} \text{ S cm}^{-1} \) at 25 °C),\(^{92}\) anti-perovskite \( \text{Li}_3\text{OCl} \) (4.82 \( \times \) \( 10^{-3} \text{ S cm}^{-1} \) at 250 °C),\(^{93}\) Nasicon \( \text{Na}_3[\text{Zr}_{2.6}\text{Ge}_{0.4}]\text{Si}_2\text{PO}_{12} \) (1.40 \( \times \) \( 10^{-2} \text{ S cm}^{-1} \) at 150 °C),\(^{94}\) perovskite \( \text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3 \) (1.0 \( \times \) \( 10^{-3} \text{ S cm}^{-1} \) at 25 °C)\(^{33}\) and thio-lisicon \( \text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{S}_4 \) (6.40 \( \times \) \( 10^{-4} \text{ S cm}^{-1} \) at 27 °C).\(^{95}\)

Further optimization of Ruddlesden-Popper compounds can lead to enhanced lithium-ion conductivity. In this work, we employed several different material design strategies to enhance the conductivities in several \( n = 2 \) or 3 Ruddlesden-Popper oxide series. Given the presence of large cations, such as \( \text{Sr}^{2+} \), in \( \text{Li}_2\text{SrTa}_2\text{O}_7 \), we hypothesized that the ionic conductivity should be enhanced if the synthesis of Ruddlesden-Popper
compounds containing smaller cations on both A and B-sites could be achieved. Cations that have smaller ionic radii will lead to smaller unit cell volumes, hence shortening the hopping distances for lithium ions. Therefore, we synthesized Li$_2$LaMTiO$_7$ (M = Ta or Nb), containing La$^{3+}$ and Ti$^{4+}$, which have smaller ionic radii than Sr$^{2+}$ and Ta$^{5+}$, respectively. In addition, we sought to enhance the ionic conductivity further by inducing defects directly in the Li-layer to improve the mobility of lithium ions, through the reduction in restrictions to ion mobility at the fully occupied lithium sites within the structure.

The results of these studies are discussed in later parts of Chapters 2 and 4 of this work. We further expanded the impact of cation-deficiency on the lithium-ion conductivity through the synthesis of a series of three-layered materials, designed systematically to have deficiencies on the A and/or A′ sites. We have shown that cation-deficiency has a major impact on the enhancement of lithium-ion conductivity in the $n = 3$ Ruddlesden-Popper oxide, Li$_{2-x}$La$_{2y}$Ti$_{3-z}$Nb$_z$O$_{10}$. Also, we demonstrate, for the first time, that intra-stack A-sites contribute to the ionic conductivity of these materials. More importantly, we have shown that lithium-ion conductivity is a result of the cooperative effect of both A and A′ sites, and a significant enhancement of conductivity can be achieved by taking advantage of this cooperative effect as discussed in Chapter 5 of this work. Following the enhancement of the overall conductivity in the $n = 2$ materials due to smaller cation size, we explored the impact of this parameter on $n = 3$ compounds, as presented in Chapters 6 and 7 of this work. Various forms of cation mixing at either A or B-site (Chapters 3 and 7) were examined in search of highly conductive Ruddlesden-Popper oxides. The findings of these studies will be discussed in detail in Chapters 2-7. While the lithium-ion conductivity still needs to be improved for practical applications, this work demonstrates
the success of the above strategies for enhancing the ionic conductivity in Ruddlesden-Popper oxides.
CHAPTER 2

INSIGHT INTO LITHIUM-ION MOBILITY IN Li$_2$La(TaTi)O$_7$

2.1 EXPERIMENTAL AND COMPUTATIONAL METHODS

The syntheses were performed by a solid-state method using powders of Li$_2$CO$_3$ (Alfa Aesar, 99.998%), La$_2$O$_3$ (Alfa Aesar, 99.99%), Ta$_2$O$_5$ (Alfa Aesar, 99.993%), and TiO$_2$ (Sigma Aldrich, 99.99%). Stoichiometric amounts of precursors were weighed and ground together. The mixtures were then pressed into pellets and calcined in alumina crucibles at 850 °C for 4 hours. The calcined pellets were ground, re-pelletized, and re-fired at 1200 °C for 6 hours in air. The heating and cooling rates in all cases were 100 °C/hour. In order to compensate for Li loss due to evaporation at high temperature, 5% extra Li$_2$CO$_3$ was added to the starting mixture. Both Li$_2$La(TaTi)O$_7$ and the A-site deficient Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ were synthesized as single-phase products. Attempts to create further A-site deficiency, beyond 0.2 moles per formula unit, led to impure products.

The work described in this chapter was published in the Journal of Materials Chemistry A, 2018, 44, 2215
The polycrystalline oxides were studied by powder X-ray diffraction (PXRD) using Cu Kα₁ radiation (λ= 1.54056 Å) in the 2θ range 5 – 100°. The crystal structures of all samples were examined by Rietveld refinements using GSAS software, and EXPGUI interface.

Microstructural characterization was performed using high-resolution field-emission scanning electron microscopy (SEM). Neutron diffraction experiments were performed on POWGEN diffractometer at Spallation Neutron Source in Oak Ridge National Laboratory at 300 K, over the d-range of 0.25 – 5 Å. Ionic conductivity measurements on sintered pellets (~1.45 mm in thickness and 9 mm in diameter) were carried out using a computer-controlled potentiostat equipped with a frequency response analyzer in the frequency range 0.1 Hz to 1 MHz and temperature range 25 to 400 °C in air. All conductivity measurements were performed under identical conditions for both the parent compound and the A-site deficient analog.

The overall computational calculations were mainly carried out employing the density functional theory (DFT) frameworks, as implemented in the Vienna Ab-initio Simulation Package (VASP). The electron-ion interactions were described by the Projector Augmented Wave (PAW), while electron exchange-correlation interactions were treated by the generalized gradient approximation (GGA) in the scheme of Perdew Burke Ernzerhof (PBE). The spin-polarized behaviors were also considered in calculations. The structural relaxation was performed using the Congregate-Gradient algorithm implemented in VASP. The micro-canonical ensemble was used in the Molecular Dynamics simulation and all atoms in the unit cell were allowed to move freely during the simulations. An energy cutoff was set at 400 eV for the plane-wave basis in all calculations, and the criteria for convergences of energy and force in relaxation processes.
were set to be $10^{-5}$ eV and $10^{-4}$ eV/Å, respectively. A 1x1x1 primitive cell was chosen and the Brillouin zones (BZ) were sampled by $5 \times 5 \times 5$ k-point meshes generated in accordance with the Monkhorst-Pack scheme in all calculations.

**Figure 2.1**: Crystal structure of Li$_2$La(TaTi)O$_7$ (left) and the tetrahedral coordination of lithium atoms (right). Green, blue, gray, and red spheres show La, Ta/Ti, Li, and O, respectively.

2.2 RESULTS AND DISCUSSION

2.3 CRYSTAL STRUCTURE

Both Li$_2$La(TaTi)O$_7$ and Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ have double-layered Ruddlesden-Popper structure type, $A_{n+1}B_nO_{3n+1}$, where $n = 2$. The double-layered Ruddlesden-Popper materials usually have tetragonal or orthorhombic structures. The common space groups are I4/mmm, P4$_2$/mmm, Fmmm, and Cmcm. For Li$_2$La(TaTi)O$_7$, the tetragonal structure is readily ruled out due to the splitting of the X-ray diffraction peaks at $2\theta = 58.8, 68.0, 77.4, 81.5, 92.8$, and $96.1^\circ$, indicating that this material
crystallizes in an orthorhombic space group. Given the angle dependence of the peak intensities in X-ray diffraction, the peaks at a high 2θ angle (low d-spacing) are not pronounced. However, this problem does not exist in neutron diffraction, which allows for careful examination of the peaks in the low d region.

![Figure 2.2: Rietveld refinement profile for powder X-ray diffraction data (a) Li$_2$La(TaTi)O$_7$ in Cmcm space group. (b) Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ in I4/mmm space group. The black crosses represent experimental data, the red line shows the fit, vertical tick marks.](image)

The neutron diffraction data show small peaks at $d = 1.115$ Å and 1.505 Å, which cannot be described by the Fmmm space group but are an excellent match with Cmcm. Figures 2.2 and 2.3 show the refinement profile for Li$_2$La(TaTi)O$_7$ using the Cmcm model with both X-ray and neutron diffraction data, respectively. The accurate determination of oxygen and lithium positions in Li$_2$La(TaTi)O$_7$ was performed using neutron diffraction.

The limitations of laboratory powder X-ray diffraction in the study of light atoms such as lithium and oxygen should be noted. These limitations can lead to the observation of unrealistic distortions in the coordination environment of lithium. However, neutron
diffraction can readily identify and study these light atoms. Table 1 lists the refined structural parameters for Li$_2$La(TaTi)O$_7$.

![Neutron diffraction profile](image)

**Figure 2.3:** Neutron diffraction Rietveld refinement profile for Li$_2$La(TaTi)O$_7$ in Cmcm space group.

Interestingly, the A-site deficiency leads to a change in the space group of Li$_2$La(TaTi)O$_7$. The A-site deficient compound, Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$, does not show the orthorhombic peak splitting discussed above. This material has a tetragonal structure, with a space group $I4/mmm$, as shown in **Figure 2.2b**. The insets in this figure highlight the difference between the powder diffraction data for Li$_2$La(TaTi)O$_7$ and the A-site deficient Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$. The refined structural parameters for Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ are listed in **Table 2.2**.

In both parent and the A-site deficient compounds, the (Ta/Ti)O$_6$ octahedra form double-layer stacks by corner-sharing. The octahedra are distorted in both compounds. The La atoms are located in spaces within the stacks, while Li atoms reside in inter-stack spaces, as shown in **Figure 2.1**. The Li atoms have distorted tetrahedral coordination geometry.
and form a layer of edge-sharing tetrahedra between the octahedral stacks. As described later, ionic conductivity occurs through this lithium layer. The scanning electron microscopy data in Figure 4 show that the microstructure of Li$_2$La(TaTi)O$_7$ remains nearly unaffected due to A-site deficiency. However, the ionic conductivity improves significantly, as discussed below.

### Table 2.1: Refined structural parameters from Rietveld refinement with powder neutron diffraction data for Li$_2$La(TaTi)O$_7$. Space group Cmcm, $a = 18.2384(5)$, $b = 5.5126(2)$, $c = 5.4996(2)$ Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{iso}$</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
<td>0</td>
<td>0.2582(4)</td>
<td>0.25</td>
<td>1</td>
<td>0.0061(2)</td>
<td>4</td>
</tr>
<tr>
<td>Ta1</td>
<td>0.1164(2)</td>
<td>0.7543(9)</td>
<td>0.25</td>
<td>0.5</td>
<td>0.0002(3)</td>
<td>8</td>
</tr>
<tr>
<td>Ti1</td>
<td>0.1164(2)</td>
<td>0.7543(9)</td>
<td>0.25</td>
<td>0.5</td>
<td>0.0002(3)</td>
<td>8</td>
</tr>
<tr>
<td>Li1</td>
<td>0.2616(3)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0136(7)</td>
<td>8</td>
</tr>
<tr>
<td>O1</td>
<td>0</td>
<td>0.6994(4)</td>
<td>0.25</td>
<td>1</td>
<td>0.0102(5)</td>
<td>4</td>
</tr>
<tr>
<td>O2</td>
<td>0.21597(9)</td>
<td>0.7803(4)</td>
<td>0.25</td>
<td>1</td>
<td>0.0088(3)</td>
<td>8</td>
</tr>
<tr>
<td>O3</td>
<td>0.6112(1)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0099(3)</td>
<td>8</td>
</tr>
<tr>
<td>O4</td>
<td>0.09107(7)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0047(2)</td>
<td>8</td>
</tr>
</tbody>
</table>
Table 2.2: Refined structural parameters from Rietveld refinement with powder X-ray diffraction data for Li\(_{1.8}\)La(Ta\(_{1.2}\)Ti\(_{0.8}\))O\(_7\). Space group: \(I4/mmm\), \(a = 3.8986(0)\) Å, \(c = 18.4520(3)\) Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>(U_{iso})</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0214(7)</td>
<td>4</td>
</tr>
<tr>
<td>Ta1</td>
<td>0</td>
<td>0</td>
<td>0.38366(9)</td>
<td>0.6</td>
<td>0.0152(6)</td>
<td>8</td>
</tr>
<tr>
<td>Ti1</td>
<td>0</td>
<td>0</td>
<td>0.38366(9)</td>
<td>0.4</td>
<td>0.0152(6)</td>
<td>8</td>
</tr>
<tr>
<td>Li1</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.9</td>
<td>0.0250</td>
<td>8</td>
</tr>
<tr>
<td>O1</td>
<td>0</td>
<td>0.5</td>
<td>0.1063(5)</td>
<td>1</td>
<td>0.022(3)</td>
<td>4</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>0</td>
<td>0.2872(7)</td>
<td>1</td>
<td>0.032(4)</td>
<td>8</td>
</tr>
<tr>
<td>O3</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>0.023(6)</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 2.4: Scanning electron microscopy data for (a) Li\(_2\)La(TaTi)O\(_7\) and (b) Li\(_{1.8}\)La(Ta\(_{1.2}\)Ti\(_{0.8}\))O\(_7\).

2.4 LITHIUM-ION CONDUCTIVITY

Variable temperature electrochemical impedance spectroscopy shows an increase in ionic conductivity as a function of temperature, as listed in Table 2.3. The impedance
plots of Li$_2$La(TaTi)O$_7$ in the Nyquist plane in the temperature range 100 – 400 °C are presented in Figure 2.5. The observed spike (tail) in the low-frequency region indicates the blocking of mobile lithium ions at the electrodes.\textsuperscript{4, 33, 38, 43, 108} The appearance of a semicircle in the high-frequency region was observed only at temperatures above 100 °C. There was no semicircle and measurable conductivity at room temperature, which can be due to the restriction of lithium-ion mobility since all lithium sites between the layers are occupied, as seen from the crystal structure in Figure 2.1. A similar behavior, i.e., lack of room temperature conductivity, was reported for the layered perovskite Li$_2$Sr$_{1.5}$Nb$_3$O$_{10}$, even though some defects had been introduced in the crystal structure.\textsuperscript{65} We will show later that, for Li$_2$La(TaTi)O$_7$, the lack of ionic conductivity at room temperature can be overcome by introducing vacancies in some lithium sites.

**Figure 2.5:** Nyquist Impedance plots for Li$_2$La(TaTi)O$_7$.  

51
The increase in conductivity with temperature is expected due to an increase in the mobility of ions and a decrease in grain boundary resistance. The total conductivity (grain and grain boundary) of Li$_2$La(TaTi)O$_7$ was determined from the intercept with the real axis in the low-frequency region of the Nyquist plot. Fitting the semicircle with only one resistance-capacitance (RC) element is not possible. This is due to the merging of two relaxation processes, occurring at similar time scales. The two processes correspond to contributions from bulk and grain boundary. To estimate these contributions, we built an electrical model as seen in the inset of Figure 2.6. Then first RC unit (R1= $1.71 \times 10^5$ and CPE1=$5.9 \times 10^{-11}$ ) correspond to the bulk (grain), and the second set (R2= $1.2 \times 10^6$ and CPE2=$3.0 \times 10^{-10}$) correspond to the grain boundary. As expected, the respective capacitance values for bulk, grain boundary, and electrode (CPE3) are in the order of $10^{-11}$, $10^{-10}$, and $10^{-7}$, respectively.

Figure 2.6: Typical fit to Nyquist Impedance plot for Li$_2$La(TaTi)O$_7$ at 200 °C.
The importance of composition design is demonstrated when \( \text{Li}_2\text{La(TaTi)O}_7 \) is compared to another compound with the same structure-type, \( \text{Li}_2\text{SrTa}_2\text{O}_7 \).\(^{43}\) The conductivity of \( \text{Li}_2\text{SrTa}_2\text{O}_7 \) has been reported at 300 °C. At this temperature, \( \text{Li}_2\text{SrTa}_2\text{O}_7 \) shows a conductivity of \( 5.0 \times 10^{-7} \text{ S cm}^{-1} \). However, at the same temperature, the conductivity value for \( \text{Li}_2\text{La(TaTi)O}_7 \) is \( 3.5 \times 10^{-6} \text{ S cm}^{-1} \), one order of magnitude greater than that of \( \text{Li}_2\text{SrTa}_2\text{O}_7 \). The enhanced conductivity of \( \text{Li}_2\text{La(TaTi)O}_7 \) can be due to the smaller ionic radii of the A-site and B-site cations in this material’s composition, leading to shorter hopping distances for \( \text{Li}^+ \). The distance between two neighboring Li-sites is as short as \( \sim 2.75 \text{ Å} \), while the same distance for \( \text{Li}_2\text{SrTa}_2\text{O}_7 \) is \( \sim 2.80 \text{ Å} \).\(^{43}\) This indicates the success of our strategy in designing \( \text{Li}_2\text{La(TaTi)O}_7 \) composition.

We also examined the effect of creating vacant sites in the Li layer by synthesizing \( \text{Li}_{1.8}\text{La(Ta}_{1.2}\text{Ti}_{0.8})\text{O}_7 \). This was done in an attempt to allow lithium ions to move more freely in the inter-stack spaces. In this material, 10% Li vacancies were introduced, and charge neutrality was maintained by changing the Ta/Ti ratio from 1/1 to 1.2/0.8. This lithium deficient compound showed significantly enhanced ionic conductivity compared to the parent \( \text{Li}_2\text{La(TaTi)O}_7 \). The conductivity values, derived from the intercept with the real axis in the low-frequency region of the Nyquist plot, are listed in Table 3. As seen here, the conductivity of the Li-deficient compound is one to two orders of magnitude greater than that of \( \text{Li}_2\text{La(TaTi)O}_7 \) at different temperatures, reaching \( 1.08 \times 10^{-3} \text{ S cm}^{-1} \) at 400 °C.
Table 2.3: Variable temperature conductivity of Li$_2$La(TaTi)O$_7$ and Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Li$_2$La(TaTi)O$_7$</th>
<th>Li$<em>{1.8}$La(Ta$</em>{1.2}$Ti$_{0.8}$)O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>N/A</td>
<td>4.08611 × 10$^{-9}$</td>
</tr>
<tr>
<td>100</td>
<td>1.82184 × 10$^{-8}$</td>
<td>2.92588 × 10$^{-7}$</td>
</tr>
<tr>
<td>200</td>
<td>1.78362 × 10$^{-7}$</td>
<td>1.45776 × 10$^{-5}$</td>
</tr>
<tr>
<td>300</td>
<td>3.50991 × 10$^{-6}$</td>
<td>1.83973 × 10$^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>2.55058 × 10$^{-5}$</td>
<td>1.034851 × 10$^{-3}$</td>
</tr>
</tbody>
</table>

Note that the Li-deficient compound shows measurable conductivity and a semicircle in the Nyquist plot even at room temperature, as shown in Figure 2.7. This semicircle could be described by three RC elements (Figure 2.8), similar to some other ionic conductors such as lithium lanthanum titanate perovskite,\textsuperscript{33, 109} where the third RC element has been assigned to electrode interface.\textsuperscript{109} As seen in Figures 2.5 and 2.7, for both compounds, the semicircles gradually shrink with an increase in temperature, and the contributions from grain and grain boundary cannot be separated. The disappearance of semicircles with an increase in temperature is commonly observed in ionic conductors such as garnets.\textsuperscript{37, 38, 110, 111}
As shown in Table 3, the conductivity of the Li-deficient compound increases significantly above room temperature, rising from $4.08 \times 10^{-9}$ to $1.08 \times 10^{-3}$ S cm$^{-1}$ at 400 °C. The activation energy for the rise in conductivity as a function of temperature can be obtained using the Arrhenius equation for thermally activated conductivity:$^{112-114}$
\[ \sigma T = \sigma_0 e^{-E_a/kT} \]

where \( \sigma_0 \) is the pre-exponential factor, characteristic of the material, and \( E_a \), \( k \), and \( T \) are the activation energy, Boltzmann constant, and the absolute temperature, respectively. The Arrhenius plots for electrical conductivity of both \( \text{Li}_2\text{La(TaTi)O}_7 \) and the Li-deficient \( \text{Li}_{1.8}\text{La(Ta}_{1.2}\text{Ti}_{0.8})\text{O}_7 \) are shown in Figure 9. The activation energy \( (E_a) \) decreases when vacancies are introduced in the lithium layers. Activation energies are 0.61 eV and 0.57 eV for \( \text{Li}_2\text{La(TaTi)O}_7 \) and \( \text{Li}_{1.8}\text{La(Ta}_{1.2}\text{Ti}_{0.8})\text{O}_7 \), respectively. The differences between the ionic conductivity of the A-site deficient and parent compound, and the large increase in conductivity due to A-site vacancies, indicate that the pathway for lithium-ion conduction is through the inter-stack layer. As discussed below, the lithium conduction pathway is confirmed by the computational study.

![Figure 2.9: Arrhenius plots for Li\textsubscript{2}La(TaTi)O\textsubscript{7} (red) and Li\textsubscript{1.8}La(Ta\textsubscript{1.2}Ti\textsubscript{0.8})O\textsubscript{7} (blue).](image)

2.5 DENSITY FUNCTIONAL THEORY CALCULATIONS

To study the lithium-ion diffusion, a DFT optimized structure was needed. Therefore, the \( \text{Li}_2\text{La(TaTi)O}_7 \) crystal structure was optimized. Various configurations with
different Ta/Ti distributions were considered. The crystalline structure for each configuration was fully relaxed and the lattice constants corresponding to each configuration were optimized. The optimized structures and the total energies corresponding to each configuration are shown in Figure 2.10. It was found that the optimized lattice constants for various configurations were the same, and within 1% of the values obtained using neutron diffraction experiments, indicating an excellent match. From comparing the total energies for different distributions of Ta and Ti, it was found that several configurations had similar energies, but among them, the first configuration in Figure 2.10 was the most favorable.

![Figure 2.10: DFT optimized structures for Li$_2$La(TaTi)O$_7$ and their corresponding total energy per unit cell. The top left configuration has the lowest energy. Gray and blue octahedra represent TaO$_6$ and TiO$_6$. Lithium atoms are shown as small spheres between.](image)

This optimized structure was used for the electronic density of states (DOS), electronic band structure, and Li-diffusion studies. In this configuration, all Ta and Ti atoms are alternately distributed within the layers and between layers, such that identical
metal atoms are separated from each other. A truly randomized distribution of Ta and Ti, similar to that determined from neutron diffraction, would require performing the calculations over hundreds or even thousands of unit cells, which is impractical. The DOS and band structure of the optimized Li$_2$La(TaTi)O$_7$ configuration are shown in Figure 2.11, the system shows a large bandgap of 2.0276 eV.

To study the degree of Li mobility in the optimized Li$_2$LaTaTiO$_7$ structure, the diffusion energy barrier was calculated along $b$- and $c$-axes directions, as shown in Figure 2.12. The diffusion energy barrier is defined as the relative energy at a particular site along the diffusion pathway with respect to the energy at the initial position. The corresponding energy barriers for the displacement of lithium by different distances from the original lithium position are shown in Figure 2.12. The energy barriers along both $b$ and $c$ directions overlap and show the same trend, indicating an isotropic Li diffusion between layers. The two peaks in Figure 2.12 indicate the high

Figure 2.11: Calculated electronic band structure (left panel) and DOS (right panel) of the optimized Li$_2$La(TaTi)O$_7$ structure. The red dashed line indicates the Fermi energy, and the insert is the Brillouin zone with special high symmetry k points.
energy barriers, where the distances between Li and O atoms become as short as ~ 1.64 Å (see insets in Figure 12). The energy barrier of ~ 1 eV is high compared to some other ionic conductors.\textsuperscript{115, 116} For example, the Li diffusion in phosphorene has an energy barrier of ~0.1 eV,\textsuperscript{117} significantly smaller than the value for Li\textsubscript{2}La(TaTi)O\textsubscript{7}. The diagonal Li diffusion in the \textit{bc} plane was also investigated, leading to huge energy barriers, in the order of 38 eV. Therefore, it is clear that lithium ions cannot diffuse in the diagonal direction. The diffusion pathway is therefore along the \textit{b} and \textit{c} directions. The main barrier to the Li diffusion along these pathways is the proximity of Li to O atoms at some positions along the conduction pathway. These results reveal that such short distances in inter-stack spaces should be eliminated to design structures with enhanced Li mobility.

\textbf{Figure 2.12:} Energy barrier as a function of displacement of Li atoms from their original sites. The insets show the structures at maximum and minimum energy barriers.
2.6 CONCLUSIONS

The study of lithium-ion mobility in Li$_2$La(TaTi)O$_7$ and its A-site deficient analog shows the potential of Ruddlesden-Popper oxides for Li-ion conductivity. The enhanced ionic conductivity of Li$_2$La(TaTi)O$_7$ and further improvement due to the A-site deficiency indicate the success of two strategies: (a) Designing compositions where Li hopping distances are shortened. (b) Creating defects in the lithium layer to enhance the mobility of lithium ions. The latter also indicates that the lithium-ion conductivity pathway is within the inter-stack spaces. This is confirmed by DFT calculations which show the direction of the pathways for lithium mobility and determine the energy barriers for each conduction pathway. These findings can be used for future research to design Ruddlesden-Popper oxides with enhanced lithium-ion conductivity.
CHAPTER 3

ENHANCING THE LITHIUM-ION CONDUCTIVITY IN Li$_2$SrTa$_{2-x}$Nb$_x$O$_7$ ($X = 0 - 2$)

3.1 EXPERIMENTAL

All material synthesis, structural refinement, and ionic conductivity measurements (~1.25 mm in thickness and 5.5 mm in diameter) follow the same approach as described in the experimental for Chapter 2. However, the pelletized samples were calcined and sintered at 1150 ºC for 10 hrs and 1150 ºC for 6hrs (with two intermittent heating).

3.2 RESULTS AND DISCUSSION

3.3 CRYSTAL STRUCTURE

Ruddlesden-Popper materials, A$_n$A′B$_n$O$_{3n+1}$, where $n = 2$, usually have tetragonal\textsuperscript{71, 81, 91, 106} or orthorhombic\textsuperscript{79, 80, 91, 107} structures with $I4/mmm$,\textsuperscript{71, 91, 106} $P4_2/mmm$,\textsuperscript{81} $Fmmm$\textsuperscript{70}, $91$ or $Cmcm$\textsuperscript{80, 107} space groups. The X-ray diffraction data for all three materials, Li$_2$SrTa$_2$O$_7$, Li$_2$SrTaNbO$_7$, and Li$_2$SrNb$_2$O$_7$, can be indexed on $Cmcm$ space group. Figure 3.2 shows the Rietveld refinement profiles for X-ray diffraction data. The refined structural

The work described in this chapter was published in Solid State Sciences, 2019, 97, 106014.
parameters are listed in Tables 3.1-3. These results are consistent with previous reports on structures of Li$_2$SrNb$_2$O$_7$ and Li$_2$SrTa$_2$O$_7$. The unit cell volume decreases slightly from 567.14(1) to 565.68(1) and 563.80(3) Å$^3$, as Ta is gradually replaced by Nb. In all three materials, there are bilayer stacks of corner-sharing BO$_6$ (B = Nb, Ta) octahedra, as shown in Figure 3.1.

Figure 3.1: Rietveld refinement profiles of powder X-ray diffraction data for (a) Li$_2$SrTa$_2$O$_7$ (b) Li$_2$SrNbTaO$_7$ and (c) Li$_2$SrNb$_2$O$_7$. Black crosses, red line, vertical tick marks, and lower blue line represent experimental data, the fit, Bragg peak positions, and the difference plot, respectively.

These stacks are separated by layers of lithium ions, which have tetrahedral coordination, as demonstrated on the right in Figure 3.1. There are two sets of non-equivalent Li–O bonds, leading to distorted LiO$_4$ tetrahedra, which are connected to each other through edge-sharing. The Sr$^{2+}$ ions reside in intra-stack spaces between NbO$_6$/TaO$_6$ octahedra. The microstructures of all three materials were examined by scanning electron microscopy on sintered pellets. As observed in Figure 3.3, the crystallite size gradually increases, as a function of Nb concentration. Given that Li$_2$SrNb$_2$O$_7$ showed the highest conductivity among this series, we decided to explore the possibility of introducing defects.
in the lithium layer, based on a hypothesis that defects can enhance the lithium-ion conductivity further.

As discussed in the next section, the defects resulted in a significant enhancement of conductivity. Neutron diffraction was utilized to determine the structure of the highly conductive Li-deficient compound. Neutron experiments are especially valuable for the accurate determination of lithium positions, which are difficult to study by laboratory powder X-ray diffraction. Interestingly, introducing defects in the inter-stack lithium layer did not alter the crystal structure, and the structural framework remained intact. Therefore, we synthesized a Li-deficient compound, Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$, where a 10 \% defect was introduced into the lithium layer. The charge balance was maintained by partial substitution of La$^{3+}$ for Sr$^{2+}$. The Li-deficient compound also crystallizes in Cmcm space group, as confirmed by Rietveld refinements with neutron and X-ray diffraction (Figure 3.4). The refined structural parameters for the Li-deficient material, Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$ are listed in Tables 3.4 and 3.5.

Table 3.1: Refined structural parameters from powder X-ray diffraction data for Li$_2$SrTa$_2$O$_7$. Space group Cmcm, $a = 18.1928(2)$ Å, $b = 5.5860(1)$ Å, $c = 5.5807(1)$ Å

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<th>$U_{iso}$</th>
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<td>8</td>
</tr>
<tr>
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<tr>
<td>O2</td>
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<tr>
<td>O3</td>
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<tr>
<td>O4</td>
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### Table 3.2: Refined structural parameters from powder X-ray diffraction data for Li$_2$SrNb$_2$O$_7$. Space group $Cmcm$, $a = 18.0004(4)$ Å, $b = 5.5994(2)$ Å, $c = 5.5938(2)$ Å
Volume = 563.80(3) Å$^3$, $Rwp = 0.0945$ $Rp = 0.0711$

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### Table 3.3: Refined structural parameters from Powder X-ray diffraction data for Li$_2$SrNbTaO$_7$. Space group $Cmcm$, $a = 18.1038(2)$ Å, $b = 5.5934(1)$ Å, $c = 5.5863(1)$ Å, Volume = 565.68(1) Å$^3$, $Rwp = 0.0945$ $Rp = 0.0820$

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<td>0.5</td>
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Figure 3.2: Typical SEM images of sintered pellets of Li$_2$SrTa$_2$O$_7$, Li$_2$SrTaNbO$_7$ and Li$_2$SrNb$_2$O$_7$.

Figure 3.3: Rietveld refinement profiles of (a) X-ray and (b) neutron diffraction data for Li$_{1.8}$Sr$_{0.8}$La$_{0.2}$Nb$_2$O$_7$. Black crosses, red line, vertical tick marks, and lower blue line
represent experimental data, the fit, Bragg peak positions, and the difference plot, respectively.

**Table 3.4:** Refined structural parameters from powder X-ray diffraction data for Li\(_{1.8}\)Sr\(_{0.8}\)La\(_{0.2}\)Nb\(_2\)O\(_7\). Space group Cmcm, \(a = 18.0862(4)\) Å, \(b = 5.5865(2)\) Å, \(c = 5.5939(2)\) Å, Volume = 565.20(3) Å\(^3\), \(R_{wp} = 0.0758\) \(R_p = 0.0574\)

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<td>0.04(1)</td>
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**Table 3.5:** Refined structural parameters from Powder neutron diffraction data for Li\(_{1.8}\)Sr\(_{0.8}\)La\(_{0.2}\)Nb\(_2\)O\(_7\). Space group Cmcm, \(a = 18.1455(5)\) Å, \(b = 5.5881(2)\) Å, \(c = 5.5828(2)\) Å, Volume = 566.10(4) Å\(^3\), \(R_{wp} = 0.0876\) \(R_p = 0.0922\)

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<th>Occupancy</th>
<th>(U_{iso})</th>
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<td>O4</td>
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<td>1</td>
<td>0.0053(6)</td>
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</table>
3.4 IONIC CONDUCTIVITY

The ionic conductivity was studied in the temperature range 25 to 500 °C using electrochemical impedance spectroscopy (EIS). Typical Nyquist plots of EIS data are shown in Figures 3.5 and 3.6. As expected from lithium-ion conductors, there is a spike (tail) in the low-frequency region, indicating the blocking of lithium ions by the electrode.\textsuperscript{3, 33, 38, 43, 108} The semicircles in impedance spectroscopy data can be fitted using combinations of resistance-capacitance (RC) elements. These RC elements describe the merging of two or three relaxation processes with similar time scales.\textsuperscript{81} The fits help to identify the bulk and grain boundary contributions to total conductivity. For example, the Nyquist plots for all three materials at 200 °C can be fitted using a model consisting of three resistance-capacitance (RC) elements, as shown in Figure 3.5. This model has been used for other ionic conductors, such as the well-known lithium lanthanum titanate perovskite,\textsuperscript{33, 109} where the third RC element is known to originate from the electrode interface.\textsuperscript{109} The first and second RC units correspond to bulk and grain boundary, respectively. At temperatures higher than 400 °C, the semicircles gradually shrink, and the
contributions from bulk and grain boundary cannot be separated. This behavior is common in ionic conductors, such as garnet-type oxides.\textsuperscript{37, 38, 110, 111}

The intercept with the real axis ($Z'$) of the Nyquist plot in the low-frequency region indicates the total resistance (bulk + grain boundary). The resistance can be used to calculate the conductivity using the relation:

$$\sigma = \frac{L}{RA}$$

where $\sigma$, $R$, $A$, and $L$ represent the total conductivity, resistance, cross-sectional surface area, and thickness of the cylindrical pellet, respectively. Among the three compounds, Li$_2$SrTa$_2$O$_7$, Li$_2$SrNbTaO$_7$, and Li$_2$SrNb$_2$O$_7$, the latter shows measurable conductivity and a semicircle at 100 °C. The other two compounds exhibit semicircles at 200 °C and higher. The absence of semicircles at low temperature has been observed in other layered compounds before, indicating low ionic mobility.\textsuperscript{65,82}

Figure 3.4: Typical fits to the Nyquist impedance plots at 200 °C (upper panels) and 300 °C (lower panels).
The activation energies for the increase in conductivity as a function of temperature can be calculated using the Arrhenius equation for thermally activated conductivity: 118, 127

$$\sigma T = \sigma^0 e^{-\frac{E_a}{kT}}$$

where $\sigma^0$, $E_a$, $k$, and $T$ represent the pre-exponential factor, which is a characteristic of the material, the activation energy, Boltzmann constant, and the absolute temperature, respectively. Figure 3.7 shows the Arrhenius plots for all three compounds, giving activation energies 0.69, 0.85 and 0.64 eV for Li$_2$SrTa$_2$O$_7$, Li$_2$SrNbTaO$_7$ and Li$_2$SrNb$_2$O$_7$, respectively.

Comparison between the conductivity of the three compounds (Table 3.6) shows that Li$_2$SrNb$_2$O$_7$ shows significantly higher conductivity than the other two materials at all temperatures of study. A systematic trend is observed, indicating the following order for conductivity:

$$\text{Li}_2\text{SrTa}_2\text{O}_7 < \text{Li}_2\text{SrNbTaO}_7 < \text{Li}_2\text{SrNb}_2\text{O}_7$$

Note that the increase in conductivity is about one order of magnitude, where conductivity values at 400 °C are $2.24 \times 10^{-6}$, $1.00 \times 10^{-5}$ and $1.22 \times 10^{-4}$ S cm$^{-1}$, for Li$_2$SrTa$_2$O$_7$, Li$_2$SrNbTaO$_7$ and Li$_2$SrNb$_2$O$_7$, respectively.
Li₂SrNbTaO₇, and Li₂SrNb₂O₇, respectively. Considering that Li₂SrNb₂O₇ showed the highest conductivity among the three compounds, we set out to enhance the conductivity of this material further. We have previously shown that Li-ion conductivity in Ruddlesden-Popper oxides occurs through the inter-stack spaces, where the lithium layer is located.⁸² We decided to examine a hypothesis, that is introducing defects in the lithium layer of Li₂SrNb₂O₇ can facilitate the mobility of Li ions, and increase the conductivity. We therefore synthesized the Li-deficient compound Li₁.₈Sr₀.₈La₀.₂Nb₂O₇ with 10% defects. Impedance spectroscopy data (Figure 3.6) indicate the success of this strategy, leading to a significant improvement in conductivity, as shown in Table 3.6. The defect compound demonstrates measurable conductivity and impedance semicircle at room temperature, where none of the three materials studied above shows measurable conductivity. In addition, the conductivity at other temperatures, up to 500 °C, is one to two orders of magnitude greater than that of the parent material at the same temperature. The improvement of conductivity due to defects in the Li-layer reconfirms that the lithium mobility takes place through the inter-stack spaces, as we have shown previously using theoretical calculations.⁸² It also shows that introducing defects can be used as an effective strategy to design Ruddlesden-Popper oxides with enhanced lithium-ion mobility.
Figure 3.6: Arrhenius plots for all compounds. The activation energies obtained from this plot are 0.69, 0.85, 0.64 and 0.44 eV for \( \text{Li}_2\text{SrTa}_2\text{O}_7 \), \( \text{Li}_2\text{SrNbTaO}_7 \), \( \text{Li}_2\text{SrNb}_2\text{O}_7 \) and \( \text{Li}_{1.8}\text{Sr}_{0.8}\text{La}_{0.2}\text{Nb}_2\text{O}_7 \), respectively.

Table 3.6: Variable temperature conductivity of Materials

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<th>( \text{Li}_2\text{SrNbTaO}_7 )</th>
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<td>N/A</td>
<td>( 7.79 \times 10^{-8} )</td>
<td>( 2.70 \times 10^{-6} )</td>
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<tr>
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<td>( 4.03 \times 10^{-8} )</td>
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<tr>
<td>300</td>
<td>( 3.42 \times 10^{-7} )</td>
<td>( 1.12 \times 10^{-6} )</td>
<td>( 2.35 \times 10^{-5} )</td>
<td>( 4.78 \times 10^{-4} )</td>
</tr>
<tr>
<td>400</td>
<td>( 2.24 \times 10^{-6} )</td>
<td>( 1.00 \times 10^{-5} )</td>
<td>( 1.22 \times 10^{-4} )</td>
<td>( 2.00 \times 10^{-3} )</td>
</tr>
<tr>
<td>500</td>
<td>( 1.08 \times 10^{-5} )</td>
<td>( 5.12 \times 10^{-5} )</td>
<td>( 4.00 \times 10^{-4} )</td>
<td>( 5.73 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

3.5 CONCLUSIONS

The investigation of lithium-ion conductivity in Ruddlesden-Popper oxides, \( \text{Li}_2\text{SrTa}_2\text{O}_7 \), \( \text{Li}_2\text{SrTaNbO}_7 \), and \( \text{Li}_2\text{SrNb}_2\text{O}_7 \), indicates a systematic increase in lithium-ion conductivity. Further enhancement of conductivity can be achieved by introducing defects in lithium layers, which are located in inter-stack spaces. The synthesis of a lithium-
deficient Ruddlesden-Popper compound, $\text{Li}_{1.8}\text{Sr}_{0.8}\text{La}_{0.2}\text{Nb}_2\text{O}_7$, which retains the crystal structure of the parent material, can be achieved. The defects help to improve the mobility of lithium-ions, leading to significantly higher conductivity in the lithium-deficient compound. These observations also confirm that the pathway for the mobility of lithium-ions in Ruddlesden-Popper compounds is through the inter-stack spaces.
CHAPTER 4

EXPERIMENTAL AND THEORETICAL INVESTIGATION OF LITHIUM-ION CONDUCTIVITY IN Li$_2$LaNbTiO$_7$

4.1 EXPERIMENTAL

All material synthesis, structural refinement, DFT calculations, and ionic conductivity measurements (~1.4 mm in thickness and ~9.0 mm in diameter) were carried out similar to the experimental description in Chapter 2. However, the pellets were heated twice at 1150 ºC for 10 hrs for 6hrs, with a heating rate of 100 ºC/h.

4.2 RESULTS AND DISCUSSION

4.3 CRYSTAL STRUCTURE

The crystal structure was studied using a combination of neutron and X-ray diffraction. Rietveld refinements were performed using GSAS software$^{118}$ and the EXPGUI interface.$^9$ The bilayer Ruddlesden-Popper compounds, A$_{n+1}$B$_n$O$_{3n+1}$, with $n$ = 2, typically crystallize in tetragonal$^{71,81,106}$ $I4/mmm$, $^{80}$ and $P4_2/mnm$, $^{81}$ or orthorhombic $\ldots$

The work described in this chapter was published in Dalton Transactions, 2019, 46, 17281.
For Li$_2$LaNbTiO$_7$, the powder X-ray diffraction peaks (Figure 4.2) could be readily indexed on Cmcm space group. The tetragonal structures were ruled out given the peak splitting at 2θ = 38.2, 58.70, 60.7, 68, 69.77.5, and 78.0° (d = 2.36, 1.57, 1.38 Å) which should be single peaks in tetragonal symmetry.

Figure 4.1: (a) Crystal structure of Li$_2$LaNbTiO$_7$. Blue, gray, and yellow spheres represent La, Nb/Ti, and Li, respectively. (b) The tetrahedral coordination environment of lithium.

Detailed structural analyses using neutron diffraction data at the low-d region revealed small peaks at $d = 1.115$ Å and 1.505 Å, which rule out the face-centering in orthorhombic symmetry, confirm the Cmcm space group. The use of neutron diffraction in structural analyses of this class of materials is essential. While the heavier atoms, such as La, Nb, and Ti, can be easily studied by X-ray diffraction, the investigation of lighter atoms, such as oxygen and lithium, by X-ray is more challenging. Indeed, the study of elements with very low atomic numbers, such as lithium, is not possible using laboratory X-ray diffraction. Whereas, such atoms can be readily investigated by neutron diffraction, as the
neutron scattering lengths and cross-sections are independent of atomic numbers. Figure 4.2b shows the Rietveld refinement profile using neutron diffraction. The structure of Li$_2$LaNbTiO$_7$ consists of bilayer stacks of (NbTi)O$_6$ octahedra (blue polyhedra in Figure 4.1), separated by lithium ions (gray spheres). The lanthanum ions (large blue spheres) occupy the available spaces within the stacks. The refined structural parameters are listed in Table 4.1.

![Figure 4.2: Rietveld refinement profile for Li$_2$LaNbTiO$_7$ in Cmcm space group. (a) Powder X-ray diffraction data. (b) Neutron diffraction data. The experimental data are represented by black crosses. The red line shows the fit, the vertical tick marks represent Bragg peak positions, and the lower blue line is the difference plot.](image)

The lithium ions, located in inter-stack spaces, form edge-sharing LiO$_4$ tetrahedra, as demonstrated in Figure 4.1b. The tetrahedra are distorted and there are two sets of lithium-oxygen bond lengths, Li-O1 = 2.0184 (× 2) and Li-O2 = 2.1043 (× 2). The edge-sharing tetrahedra for two-dimensional layers in the bc plane. As will be discussed later, the Li-mobility takes place through these layers. We postulated that creating free spaces for lithium ions within these layers can enhance lithium-ion mobility.
We, therefore, synthesized the lithium-deficient analog, Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$, to study this effect. In this material, there is 10% Li-deficiency, and the charge balance is maintained by changing the Nb/Ti ratio. The defect material has the same crystal structure as the parent material, as described above (Table 4.2). The microstructures observed in scanning electron microscopy images (Figure 3) show a small increase in the crystallite size for the Li-deficient material.

**Table 4.1:** Structural parameters from Rietveld refinement using neutron diffraction data for Li$_2$LaNbTiO$_7$. Space group Cmcm, $a = 18.2068$ Å, $b = 5.5150(2)$ Å, $c = 5.5040(2)$ Å, $R_p = 0.0394$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
<td>0</td>
<td>0.2595(4)</td>
<td>0.25</td>
<td>1</td>
<td>0.0052(2)</td>
<td>4</td>
</tr>
<tr>
<td>Li1</td>
<td>0.2628(3)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0150(7)</td>
<td>8</td>
</tr>
<tr>
<td>Nb1</td>
<td>0.1178(2)</td>
<td>0.7509(8)</td>
<td>0.25</td>
<td>0.5</td>
<td>0.00040(3)</td>
<td>8</td>
</tr>
<tr>
<td>Ti1</td>
<td>0.1178(2)</td>
<td>0.7509(8)</td>
<td>0.25</td>
<td>0.5</td>
<td>0.00040(3)</td>
<td>8</td>
</tr>
<tr>
<td>O1</td>
<td>0</td>
<td>0.6981(4)</td>
<td>0.25</td>
<td>1</td>
<td>0.0108(5)</td>
<td>4</td>
</tr>
<tr>
<td>O2</td>
<td>0.2164(9)</td>
<td>0.7804(4)</td>
<td>0.25</td>
<td>1</td>
<td>0.0104(3)</td>
<td>8</td>
</tr>
<tr>
<td>O3</td>
<td>0.6114(1)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0107(3)</td>
<td>8</td>
</tr>
<tr>
<td>O4</td>
<td>0.0911(7)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0051(2)</td>
<td>8</td>
</tr>
</tbody>
</table>

**Table 4.2:** Structural parameters from Rietveld refinement using X-ray diffraction data for Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$. Space group Cmcm, $a = 18.3608(2)$ Å, $b = 5.51830(1)$ Å, $c = 5.5182(1)$ Å, $R_p = 0.888$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
<td>0</td>
<td>0.2543(10)</td>
<td>0.25</td>
<td>1</td>
<td>0.024(1)</td>
<td>4</td>
</tr>
<tr>
<td>Li1</td>
<td>0.2628</td>
<td>0</td>
<td>0</td>
<td>0.9</td>
<td>0.0250</td>
<td>8</td>
</tr>
<tr>
<td>Nb1</td>
<td>0.1168(12)</td>
<td>0.7512(10)</td>
<td>0.25</td>
<td>0.6</td>
<td>0.017(1)</td>
<td>8</td>
</tr>
<tr>
<td>Ti1</td>
<td>0.1168(12)</td>
<td>0.7512(10)</td>
<td>0.25</td>
<td>0.4</td>
<td>0.0159(8)</td>
<td>8</td>
</tr>
<tr>
<td>O1</td>
<td>0</td>
<td>0.750(9)</td>
<td>0.25</td>
<td>1</td>
<td>0.018(8)</td>
<td>4</td>
</tr>
<tr>
<td>O2</td>
<td>0.2147(6)</td>
<td>0.769(5)</td>
<td>0.25</td>
<td>1</td>
<td>0.029(5)</td>
<td>8</td>
</tr>
<tr>
<td>O3</td>
<td>0.6060(17)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.09(1)</td>
<td>8</td>
</tr>
<tr>
<td>O4</td>
<td>0.0955(12)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.003(6)</td>
<td>8</td>
</tr>
</tbody>
</table>
4.4 IONIC CONDUCTIVITY

The ionic conductivity was investigated by electrochemical impedance spectroscopy over a range of frequencies and temperatures. This technique offers an opportunity for the separation of the contributions that arise from the grain, grain boundary, and electrode properties. When modeled in terms of equivalent electrical circuits, this technique offers an understanding of transport processes taking place in the material.\cite{81,108}

The complex impedance is expressed as $Z^* = Z' - jZ''$, where $Z'$ and $Z''$ represent the real and imaginary axes of the plot respectively. These parts can be expressed as:\cite{121}

$$Z' = \frac{R_g}{1+(\omega R_g C_g)^2} + \frac{R_{gb}}{1+(\omega R_{gb} C_{gb})^2}, \quad Z'' = \frac{R_g}{1+(\omega R_g C_g)^2} + \frac{R_{gb}}{1+(\omega R_{gb} C_{gb})^2}$$  \hspace{1cm} (1)

where $\omega = \text{angular frequency}$, $R_g = \text{grain resistance}$, $R_{gb} = \text{grain boundary resistance}$, $C_g = \text{grain capacitance}$ and $C_{gb} = \text{grain boundary capacitance}$. Figures 4.4 and 4.5 show typical
impedance data for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ in Nyquist plots. The semicircles in these plots represent the relaxation processes in the material, as will be discussed later. The observed spike (tail) in the low-frequency region is an indication of the blocking of mobile lithium ions at the electrode interface, a property that is commonly observed in ionic conductors.$^4, ^{33, 37, 38, 43, 108}$ The total resistance can be determined from the intercept with the real axis ($Z'$) in Nyquist plots, as shown in Figures 4.4 and 4.5. However, it is also possible to distinguish the bulk and grain-boundary contributions to the total resistance. The nature of the semicircle in impedance data can be described based on the merging of two relaxation processes, related to the bulk and grain boundary, occurring at time scales that are not significantly different.$^{81, 121}$

**Figure 4.4:** Typical Nyquist Impedance plots for Li$_2$LaNbTiO$_7$. 
In order to estimate the contribution of each, we used a resistance-capacitance (RC) model consisting of a series of two RC units, as seen in the inset of Figures 4.4 and 4.5, where R1 and R2 represent the polarization resistances for bulk and grain boundary, respectively. The CPE components represent the constant phase elements, which model the capacitance behavior in bulk (CPE1), grain-boundary (CPE2), and electrode interface (CPE3). The latter is used for modeling the observed tail in the data, corresponding to the lithium blocking at the electrode surface. As a typical example, the fits for Li$_2$LaNbTiO$_7$ data at 100 °C give $R_1 = 3.341 \times 10^6$ Ω, CPE1 = $5.998 \times 10^{-11}$ F, $R_2 = 1.038 \times 10^7$ Ω, CPE2 = $1.995 \times 10^{-10}$ F, and CPE3 = $5.937 \times 10^{-7}$ F. The CPE values are consistent with those expected for bulk, grain boundary, and electrode surface polarization, which should be in the order of $10^{-11}$ F, $10^{-10}$ F, and $10^{-7}$ F, respectively.

The total resistance ($R$) obtained from the impedance data is used to calculate the conductivity ($\sigma$) using $\sigma = L/RA$, where $L$ represents the thickness and $A$ is the cross-sectional area of the cylindrical pellet, used for these measurements. Li$_2$LaNbTiO$_7$ shows detectable conductivity and a semicircle at temperatures higher than 100 °C. The lack of
room temperature conductivity has been observed in the previously reported compound, Li$_2$SrTa$_2$O$_7$ as well.\textsuperscript{43} However, when compared to Li$_2$SrTa$_2$O$_7$,\textsuperscript{43} our material shows higher conductivity by nearly two orders of magnitude. For Li$_2$SrTa$_2$O$_7$, the conductivity is reported at 300 ºC. Therefore, we compare the conductivities at this temperature, which are $5.0 \times 10^{-7}$ S cm$^{-1}$ for Li$_2$SrTa$_2$O$_7$\textsuperscript{43} and $2.150 \times 10^{-5}$ S cm$^{-1}$ for Li$_2$LaNbTiO$_7$. The enhanced conductivity of Li$_2$LaNbTiO$_7$ indicates the success of our material design strategy, i.e., compressing the unit cell and shortening the Li-Li hopping distance through the incorporation of ions with smaller ionic radii in the material composition. The ionic radii of La$^{3+}$ (1.36 Å) and Ti$^{4+}$ (0.605 Å) are smaller than those of Sr$^{2+}$ (1.44 Å) and Ta$^{5+}$ (0.64 Å), respectively.\textsuperscript{122} A comparison between the two materials shows the shortening of Li-Li separation in Li$_2$LaNbTiO$_7$, where these distances can be as short as ~ 2.75 Å, as compared to ~ 2.80 Å for Li$_2$SrTa$_2$O$_7$.

Given our prior experience,\textsuperscript{82} we postulated that the lithium-ion conductivity can be enhanced further if vacancies were created in the lithium layer to allow more facile mobility of lithium ions. This strategy was proven successful through the synthesis and investigation of Li$_{1.8}$La$_{1.2}$Nb$_{0.8}$Ti$_{0.2}$O$_7$, which showed enhanced lithium-ion conductivity. The impedance data for this compound has a semicircle and detectable conductivity at room temperature. As shown in Table 4.3, the Li-deficient compound shows significantly enhanced conductivity, which is several times greater than that of the parent non-deficient material. The observed trend is similar to that of the Ta-analogue, which we reported previously.\textsuperscript{82} The increase in lithium-ion conductivity due to defects in the lithium-layer (Figure 4.1b) indicates that Li mobility pathways in this class of compounds are through the Li-layer in $bc$ plane.
This was also confirmed by density functional theory calculation, as discussed later. The increase in temperature leads to a gradual increase in conductivity, as expected, due to the enhanced mobility of lithium ions at a higher temperature, eventually reaching \( \sim 10^{-3} \text{ S cm}^{-1} \) at 500 °C. A gradual shrinking of the semicircle is observed as temperature increases, a feature that is commonly observed in ionic conductors.\(^{37, 38, 110, 111}\) It is noted that the Li-ion conductivity of these materials is still not enough for practical application. Some solid Li-ion conductors such as garnets show conductivity in the order of \( 10^{-4} \text{ S cm}^{-1} \) at room temperature.\(^{18, 20}\)

**Table 4.3:** Variable temperature conductivity of \( \text{Li}_2\text{LaNbTiO}_7 \) and \( \text{Li}_{1.8}\text{LaNb}_{1.2}\text{Ti}_{0.8}\text{O}_7 \)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \text{Li}_2\text{LaNbTiO}_7 )</th>
<th>( \text{Li}<em>{1.8}\text{LaNb}</em>{1.2}\text{Ti}_{0.8}\text{O}_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>N/A</td>
<td>( 4.258 \times 10^{-9} )</td>
</tr>
<tr>
<td>100</td>
<td>( 2.360 \times 10^{-8} )</td>
<td>( 1.241 \times 10^{-7} )</td>
</tr>
<tr>
<td>200</td>
<td>( 1.310 \times 10^{-6} )</td>
<td>( 4.584 \times 10^{-6} )</td>
</tr>
<tr>
<td>300</td>
<td>( 2.150 \times 10^{-5} )</td>
<td>( 8.063 \times 10^{-5} )</td>
</tr>
<tr>
<td>400</td>
<td>( 1.450 \times 10^{-4} )</td>
<td>( 4.960 \times 10^{-4} )</td>
</tr>
<tr>
<td>500</td>
<td>( 5.731 \times 10^{-4} )</td>
<td>( 1.780 \times 10^{-3} )</td>
</tr>
<tr>
<td>600</td>
<td>( 1.626 \times 10^{-3} )</td>
<td>( 4.713 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

A plot of the temperature dependence of the conductivity of both materials based on the Arrhenius equation is shown in Figure 4.6. The activation energies for the thermally activated conductivities were calculated from the Arrhenius equation:\(^{82}\)

\[
\log\sigma_T = \log\sigma_0 - \left( \frac{E_a}{2.303kT} \right)
\]  \hspace{1cm} (2)
where $\sigma_0$ is a pre-exponential factor, characteristic of the material, and $E_a$, $k$, and $T$ are the activation energy, Boltzmann constant, and the absolute temperature respectively. The calculated activation energies were 0.676 and 0.647 eV for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$, respectively. The thermal activation energies are similar, and the enhanced conductivity of Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ is a result of vacancies in the lithium layer.

The variation of the real part of impedance ($Z'$) as a function of angular frequency over a range of temperatures for both compounds is shown in Figures 4.7. There is a decrease in $Z'$ as the frequency increases. This is a common behavior, and could indicate the lowering of energy barriers and enhanced conductivity across grain-boundary at high frequency. Also, there is a significant decrease in $Z'$ with temperature, consistent with the negative temperature coefficient of resistance in these materials. Figure 4.8 shows the variation of the imaginary part of impedance ($Z''$) as a function of angular frequency at different temperatures. A broad peak is observed, which

![Arrhenius plot for Li$_2$LaNbTiO$_7$ (black squares) and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ (blue triangles).](image)

**Figure 4.6:** Arrhenius plot for Li$_2$LaNbTiO$_7$ (black squares) and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ (blue triangles).
eventually flattens as temperature increases, a common behavior for the imaginary part of impedance.\textsuperscript{121, 125-127}

The occurrence of this peak indicates the presence of immobile species at low temperature,\textsuperscript{127} which become mobile as temperature increases. The disappearance of the peak and the overall decrease in the magnitude of $Z''$ at higher temperatures confirm the temperature dependence of relaxation phenomena.\textsuperscript{42-44} Importantly, a comparison between the $Z''$ peaks of Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ indicates that the peak for the latter is shifted toward higher frequency, which implies an increase in the rate of hopping of localized charge carriers,\textsuperscript{121} as

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{impedance_data.png}
\caption{Real part of impedance data as a function of angular frequency ($Z'$ vs log $\omega$) for (a) Li$_2$LaNbTiO$_7$ and (b) Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.}
\end{figure}
Figure 4.8: Imaginary part of impedance data as a function of angular frequency ($Z''$ vs log $\omega$) for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.

expected considering that defects created in the Li-layer of Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ enhance the Li-ion mobility. The dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) are also calculated using the following equations:

$$\varepsilon' = \frac{t}{\omega A \varepsilon_0} \cdot \frac{-Z''}{Z'^2 + Z''^2} \quad \varepsilon'' = \frac{t}{\omega A \varepsilon_0} \cdot \frac{Z'}{Z'^2 + Z''^2} \quad \tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (3)$$

where $A$ is the cross-sectional area of the sample, $t$ is the thickness of the sample, $\varepsilon_0$ is the permittivity of free space, $Z'$ is the real part of impedance and $Z''$ is the imaginary part of impedance.\textsuperscript{121, 129, 130} There are minor variations in the literature about the formula used for dielectric constant ($\varepsilon'$). The negative sign in the numerator is sometimes shown\textsuperscript{46, 47} and sometimes absent.\textsuperscript{121} Also, some researchers have represented the $t/A\varepsilon_0$ part as the inverse of capacitance $1/C_0$.\textsuperscript{46, 47}

Figure 4.9 shows dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) as a function of frequency at different temperatures for both compounds. There is a decrease in the dielectric constant as the frequency increases, which indicates the inability of electric dipoles to conform to the fast reversal of the AC electric field at high frequency.\textsuperscript{20, 121} This
behavior is typical of ionic conducting materials. At high frequencies, the oscillating charge carriers can not contribute significantly to the dielectric constant, and the dielectric properties arise from electronic polarization. The larger dielectric constant at low frequency arises from dipolar and interfacial polarization (i.e., Maxwell–Wagner–Sillar polarization). The dielectric constant values increase at a higher temperature, as the mobility of thermally activated charge carriers and the reorientation of dipoles is facilitated by an increase in temperature.

Figure 4.9: Temperature and frequency dependence of (a) dielectric constant ($\epsilon'$) and (b) dielectric loss (tan $\delta$) for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.

Also, at higher temperatures, the plateau in the dielectric constant plot is shifted to a higher frequency, indicating that the dipolar polarization is thermally activated. The dielectric loss (tan $\delta$) occurs due to the dissipation of the electrical energy that would otherwise be used to induce polarization in the material. The plot of tan $\delta$ versus
frequency shows a peak, similar to that observed in other ionic conductors. The peak shifts to a higher frequency as temperature increases, indicating the enhancement in the mobility of charge carriers. Importantly, a comparison between the dielectric loss peaks for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ shows that the peak for Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ appears at a higher frequency, further confirming the enhanced mobility of lithium-ions in Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.

The complex modulus spectra (M' versus M'') for the ion transport phenomena at different temperatures in both compounds is shown in Figure 4.10. The modulus analysis can be used as a tool for exploring the dynamic aspects of charge transport such as ion/carrier hopping rates and relaxation times of conductivity. The electrical modulus in terms of complex modulus function can be expressed as: $M^* = M' + j M''$. The real and imaginary components of the complex modulus can be described as:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}, \quad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2},$$

where $\varepsilon'$ and $\varepsilon''$ are the real and the imaginary components of dielectric permittivity, respectively.
The complex modulus spectra of $M''$ versus $M'$ for the parent and the lithium-deficient material are shown in Figure 4.10. In addition, the variation of real ($M'$) and imaginary ($M''$) parts of modulus as a function of frequency at different temperatures is shown in Figure 4.11. As observed from the variation of the real part as a function of frequency at selected temperatures, $M'$ tends to be very small, close to zero, in the lower frequency region. As frequency increases, there is an increase and dispersion in $M'$. The observed dispersion may be the result of the short-range mobility of charge carriers. The plot patterns also show a variation of $M'$ as a function of temperature, which indicates the temperature-dependence of relaxation processes in these materials.\textsuperscript{32,34,43}
Figure 4.11: Variations of real (M') and imaginary (M'') parts of Modulus with temperature over different frequency ranges for Li$_2$LaNbTiO$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$.

The plot of M'' versus frequency shows a peak, which shifts towards higher frequency as temperatures rise. This indicates the correlated motion of mobile ions\textsuperscript{34} and once again confirms the temperature-dependence of ionic mobility. The peak frequency is indicative of a transition from long-range (below the peak) to short-range (above the peak frequency) ionic mobility.\textsuperscript{43} The broad asymmetric shape of the peak is suggestive of a non-Debye type relaxation with different time constants.\textsuperscript{34,43}

4.5 DENSITY FUNCTIONAL THEORY CALCULATIONS

The DFT calculations were utilized to examine the lithium conduction pathways in this series of compounds. The energy barrier for lithium diffusion in Li$_2$LaNbTiO$_7$ was investigated. The band structure and density of states were also calculated, showing a large bandgap of 2.086 eV, as shown in Figure 4.12. The mobility of lithium-ion in different directions in Li$_2$LaNbTiO$_7$ was examined and the energy associated with each pathway
was calculated. In these calculations, lithium ions were gradually displaced from their lattice position, and the change in the energy of the system was computed at different distances in a particular direction. The lithium hopping in the $x$-direction (parallel to the unit cell axis $a$) is unrealistic given the long separation (~10 Å) between lithium layers in the $a$-direction. Therefore, the energy barrier for lithium mobility in $\text{Li}_2\text{LaNbTiO}_7$ was calculated for $b$ and $c$-directions. It was found that in this material, the energy barriers in both directions are identical.

Figure 4.13 shows the graph of diffusion energy versus lithium displacement in the $b$-direction. The diffusion energy is defined as the energy of the system relative to the state where Li-ions are in their original position. As demonstrated in this figure, the displacement of lithium from its original position leads to an increase in the energy of the system, which reaches a peak at ~1.5 Å. As shown in the inset of Figure 4.13, the energetic bottleneck is associated with the proximity of lithium ions to oxygens located above and below the lithium layer. The close interaction of lithium and oxygen drives the energy of the system higher. The energy barrier of ~1 eV is high compared to some other ionic conductors,$^{115-117}$ where the energy bottleneck can be as small as ~0.1 eV.$^{50}$
Figure 4.12: Calculated electronic band structure and density of states (DOS) for Li$_2$LaNbTiO$_7$. The red dashed line shows the Fermi energy. The Brillouin zone with special high symmetry k points is shown in the inset.

For comparison, the diffusion energy was also calculated for Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ in $b$-direction. As shown in Figure 4.13, the diffusion energy for the Li-deficient compound follows the same trend as the parent material, reaching a peak at \(~ 1.5 \, \text{Å} \) for Li displacement. There is a slight decrease in the energy barrier for the Li-deficient compound compared to the parent material.

The information obtained from DFT calculations can be helpful in designing materials with higher Li conductivity. These results show that the proximity of lithium and oxygen in the bottleneck is the main reason for the high energy barrier. Therefore, one may envision the possibility of lowering the energy barrier by increasing the separation of the octahedral stacks (Figure 1), which can lead to longer distances between oxygen and lithium ions located between the stacks. This may result in better mobility of lithium ions and lower diffusion energy.
Figure 4.13: Energy barrier as a function of lithium displacement in b-direction for Li$_2$LaNbTiO$_7$ (black circles) and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$ (red squares). The insets show the structures at the maximum and minimum energies.

4.6 CONCLUSIONS

The shortening of lithium hopping distances by incorporation of cations with smaller ionic radius in the Ruddlesden-Popper structure can lead to the enhancement of lithium-ion conductivity, as shown in Li$_2$LaNbTiO$_7$, compared to Li$_2$SrTa$_2$O$_7$. Furthermore, the creation of defects in the inter-stack lithium layer can enhance the conductivity further, as demonstrated through the synthesis and investigation of Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$. The direction of lithium diffusion is parallel to the unit cell axes $b$ and $c$. The energy barrier for lithium diffusion is associated with the proximity of lithium and oxygen atoms. This information may be used for the future design of Li-conducting Ruddlesden-Popper oxides, where wider separation of stacks can prevent the proximity of lithium and oxygen, leading to the lowering of the energy barrier for lithium diffusion.
CHAPTER 5

STRATEGIES FOR ENHANCING LITHIUM-ION CONDUCTIVITY OF TRIPLE-LAYERED RUDDLESDEN-POPPER OXIDES: CASE STUDY OF

\[ \text{Li}_{2-x}\text{La}_{2-y}\text{Ti}_{3-z}\text{Nb}_{z}\text{O}_{10} \]

5.1 EXPERIMENTAL

All material synthesis, structural refinement, neutron diffraction experiments, and ionic conductivity measurements were carried out similar to the procedure described in Chapter 2 above. The pellets were calcined at 550 °C for 12 hours and sintered at 1200 °C for 3 hours in air (heating and cooling rate of 2 °C/min). Lithium loss due to evaporation at high temperature was compensated for by adding 15% extra Li\(_2\)CO\(_3\), at the beginning of each synthesis. The most lithium-deficient compound, \(\text{Li}_{1.75}\text{La}_{2.75}\text{Ti}_{2.75}\text{Nb}_{0.25}\text{O}_{10}\), was studied by X-ray photoelectron spectroscopy (Figure 5.2).

The work described in this chapter was published in Inorganic Chemistry, 2020, 59, 9718
5.2 RESULTS AND DISCUSSION

5.3 CRYSTAL STRUCTURE

Crystal structures of the synthesized materials (Figure 5.1) were investigated by neutron and X-ray diffraction. Representative examples of refined structural parameters using neutron diffraction for materials with the highest degrees of cation-deficiency are shown in Tables 5.1 and 5.2.

![Figure 5.1: Crystal structure of triple-layered Ruddlesden-Popper oxide, A_2A_2'B_3O_{10} (A = Li, A’=La, B = Ti/Nb). (a) The BO_6 octahedra are shown in green, with blue and yellow spheres representing La and Li, respectively. (b) The LaO_{12} and LiO_4 polyhedral are shown in blue and purple, respectively.](image-url)
Figure 5.2: X-ray photoelectron spectroscopy data for Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$. The binding energies are consistent with trivalent lanthanum (a), pentavalent niobium (b), and tetravalent titanium (c).\cite{131}

There is one report on the structure of Li$_2$La$_2$Ti$_3$O$_{10}$,\cite{132} indicating the formation of a tetragonal $I4/mmm$ structure, as commonly observed in triple-layered Ruddlesden-Popper oxides.\cite{133-135} Our Rietveld refinements (Figure 5.3) confirmed this structure for Li$_2$La$_2$Ti$_3$O$_{10}$. The crystal structure consists of three layers of corner-sharing (Ti/Nb)O$_6$ octahedra, which form stacks, separated by lithium ions (purple spheres in Figure 1) that are located in inter-stack spaces and have tetrahedral coordination. The LiO$_4$ tetrahedra are connected to each other through edge-sharing. There are also intra-stack spaces between the octahedra, which are occupied by lanthanum ions (blue spheres) that are 12-coordinated.
Table 5.1: Structural parameters from Rietveld refinement using powder neutron diffraction data for Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$. Space group I$4/mmm$, $a = 3.8457(1)$ Å, $b = 3.8457(1)$ Å, $c = 26.563(1)$ Å, $R_p = 0.0654$, $R_wp = 0.0635$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
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<td>0.4195(1)</td>
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<td>0.81(6)</td>
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<td>4</td>
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<tr>
<td>Ti1</td>
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<td>0.1587(3)</td>
<td>0.93(1)</td>
<td>0.009(1)</td>
<td>4</td>
</tr>
<tr>
<td>Nb1</td>
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<td>0</td>
<td>0.1587(3)</td>
<td>0.07(1)</td>
<td>0.009(1)</td>
<td>4</td>
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<tr>
<td>Ti2</td>
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<td>0</td>
<td>0</td>
<td>0.97(1)</td>
<td>0.009(1)</td>
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<tr>
<td>Nb2</td>
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<td>0</td>
<td>0.03(1)</td>
<td>0.009(1)</td>
<td>2</td>
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<tr>
<td>O1</td>
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<td>1</td>
<td>0.0127(8)</td>
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<tr>
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<td>0.1452(1)</td>
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<td>0.0085(4)</td>
<td>8</td>
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<tr>
<td>O3</td>
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<td>0.0726(2)</td>
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<tr>
<td>O4</td>
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<td>0.090(5)</td>
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</table>

The corner-sharing octahedral layers are stacked along the c-direction, and each triple-layer stack is shifted relative to its nearest neighbors above and below. The alternating fashion of stacking of triple-layer octahedral blocks leads to large distortions in the outer layer octahedra compared with the octahedra in the inner layer of each stack.\textsuperscript{135} Given the restrictions to lithium-ion mobility in this class of materials,\textsuperscript{43, 65, 82} we set out to determine the effect of cation-deficiency on ionic conductivity, based on the hypothesis that cation-deficiency on specific sites can reduce the restrictions to the mobility of lithium ions.
Table 5.2: Structural parameters from Rietveld refinement using powder neutron diffraction data for $\text{Li}_2\text{La}_{1.8}\text{Ti}_{2.4}\text{Nb}_{0.6}\text{O}_{10}$. Space group $I4/mmm$, $a = 3.8629(2)$ Å, $b = 3.8629(2)$ Å, $c = 26.319(2)$ Å, $R_p = 0.0550$, $Rwp = 0.0543$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Multiplicity</th>
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</tr>
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<td>0.020(3)</td>
<td>4</td>
</tr>
<tr>
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<td>0.1622(7)</td>
<td>0.774(9)</td>
<td>0.031(4)</td>
<td>4</td>
</tr>
<tr>
<td>Nb1</td>
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<td>0</td>
<td>0.1622(7)</td>
<td>0.226(9)</td>
<td>0.031(4)</td>
<td>4</td>
</tr>
<tr>
<td>Ti2</td>
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<td>0</td>
<td>0</td>
<td>0.97(1)</td>
<td>0.031(4)</td>
<td>2</td>
</tr>
<tr>
<td>Nb2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.03(1)</td>
<td>0.031(4)</td>
<td>2</td>
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<tr>
<td>O1</td>
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<td>0.1454(1)</td>
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</tr>
<tr>
<td>O3</td>
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<td>0.0733(2)</td>
<td>1</td>
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<tr>
<td>O4</td>
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<td>0.5</td>
<td>0</td>
<td>1</td>
<td>0.080(4)</td>
<td>4</td>
</tr>
</tbody>
</table>

We, therefore, synthesized six materials, containing systematic cation-deficiencies on A/A’-sites. All six compounds were found to be isostructural to $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, as discussed below. To investigate the effect of cation-deficiency in the A-site, where Li is located, we synthesized three materials with 5%, 10% and 12.5% lithium deficiency, namely $\text{Li}_{1.9}\text{La}_2\text{Ti}_{2.9}\text{Nb}_{0.1}\text{O}_{10}$, $\text{Li}_{1.8}\text{La}_2\text{Ti}_{2.8}\text{Nb}_{0.2}\text{O}_{10}$, and $\text{Li}_{1.75}\text{La}_2\text{Ti}_{2.75}\text{Nb}_{0.25}\text{O}_{10}$. The latter material represents the limit of cation-deficiency on the A-site. Materials with a higher degree of A-site deficiency cannot be synthesized as single-phase products. The charge neutrality is maintained by partial replacement of Ti$^{4+}$ by Nb$^{5+}$. As will be discussed later, systematic improvements in lithium-ion conductivity were observed as a function of A-site deficiency. The charge balance is also confirmed from the oxidation states of the most deficient lithium material, $\text{Li}_{1.75}\text{La}_2\text{Ti}_{2.75}\text{Nb}_{0.25}\text{O}_{10}$ using XPS (Figure 5.1). All A-site deficient materials showed the same crystal structure as $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, as shown in Figure 5.3. There is a systematic increase in unit cell volume as more A-site deficiency and more
Nb$^{5+}$ are incorporated into the material structure, as determined by high-resolution X-ray diffraction. The unit cell volume of Li$_2$La$_2$Ti$_3$O$_{10}$ is 390.95(2) Å$^3$, as compared with 391.41(1) Å$^3$, 392.34(2) Å$^3$, and 393.82(2) Å$^3$ for the A-site deficient materials, respectively. This is due to the larger ionic radius of Nb$^{5+}$ compared with Ti$^{4+}$. The material with the highest degree of A-site deficiency, Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$, was also examined by neutron diffraction (Figure 5.4), which helped with the accurate determination of the position and site occupancy of lithium.

Neutron diffraction is a more reliable technique than laboratory X-ray diffraction for the study of the position of light atoms such as lithium. The neutron diffraction results were in agreement with expected values, as shown in Table 5.1. The effect of cation-deficiency in the A′-site, where lanthanum is located, on ionic conductivity, was also investigated. This was done through the synthesis of Li$_2$La$_{1.9}$Ti$_{2.7}$Nb$_{0.3}$O$_{10}$ and Li$_2$La$_{1.8}$Ti$_{2.4}$Nb$_{0.6}$O$_{10}$, where the latter represents the limit of A′-site deficiency. These materials are isostructural to Li$_2$La$_2$Ti$_3$O$_{10}$ and the A-site deficient compounds (Figure 5.3). Again, a systematic increase in unit cell volume is observed in the A′-site deficient materials, which show cell volumes of 392.37(1) and 393.29(1) Å$^3$. The material with the highest A′-site deficiency was also investigated with neutron diffraction (Figure 5.4), which gave results matching the expected values, as shown in Table 5.3.
Figure 5.3: Rietveld refinement profiles using X-ray diffraction data in I4/mmm space group for: (a) Li$_2$La$_2$Ti$_3$O$_{10}$. (b) Li-deficient compounds Li$_{1.9}$La$_2$Ti$_{2.9}$Nb$_{0.1}$O$_{10}$, Li$_{1.8}$La$_2$Ti$_{2.8}$Nb$_{0.2}$O$_{10}$, and Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$. (c) La-deficient compounds, Li$_2$La$_{1.9}$Ti$_{2.7}$Nb$_{0.3}$O$_{10}$ and Li$_2$La$_{1.8}$Ti$_{2.4}$Nb$_{0.6}$O$_{10}$. (d) Both Li- and La-deficient compound, Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. 
Finally, to investigate the cooperative effect of both A and A’-sites, the cation-deficient compound, Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$ was synthesized, featuring deficiency on both lithium and lanthanum sites. This material represents the limit of simultaneous deficiency distributed equally on both A and A’-sites. This compound was also found to be isostructural to the above materials (Figure 5.3) and showed the highest lithium-ion conductivity of all the compounds studied in this work, as will be discussed in detail in the next section.

5.4 IONIC CONDUCTIVITY

The ionic conductivity of all seven materials was studied using electrochemical impedance spectroscopy (EIS). The highly coupled transport processes occurring in the grain, grain boundary, and electrolyte/electrode interfaces can be distinguished EIS.\textsuperscript{81, 108, 136} It can also be used for the determination of the relaxation frequency, capacitance, and
electrical conductivity. For all measured compounds, the impedance spectra (Figure 5.5) consist of a semicircle and a spike at lower temperatures, with gradual shrink of the semicircle at higher temperatures owing to the increase in ion mobility. The spike (tail) indicates the blocking of mobile lithium ions by the electrode and is commonly observed in lithium-ion conductors. At higher temperatures the intercept of the spike on the real axis draws closer to the origin, which is characteristic of reduction in the resistance of the material. The appearance of a semicircle in the high-frequency region of the Nyquist plot represents relaxation processes taking place in the material. The semicircles can be modeled by electrical circuits to reveal the electrical behavior and contribution of different components to ionic diffusion.

The total resistance (R) is determined from the intercept of the spike in the Nyquist plot with the real axis (Z’). The conductivity is then calculated using the equation: \( \sigma = \frac{L}{RA} \), where \( L \) is the thickness of the sample and \( A \) is the cross-sectional area of the sintered pellet. The contributions of the resistance within the grain, and in grain boundaries are obtained using the electrical circuit models. Li2La2Ti3O10 showed no measurable conductivity at room temperature, but at a higher temperature, above 200 °C, a semicircle and measurable conductivity were observed. Figure 5.5 shows representative examples of impedance spectra at 200 °C for all materials for direct comparison. This lack of measurable conductivity for Li2La2Ti3O10 at room temperature can be attributed to the restriction of the mobility of lithium ions, due to the lack of available hopping sites.

To address this issue, materials containing defects in the lithium layer (A-site) were synthesized, leading to exponential improvement in lithium-ion conductivity. The conductivity was enhanced systematically as the degree of A-site deficiency was increased:
$\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} < \text{Li}_{1.9}\text{La}_2\text{Ti}_{2.9}\text{Nb}_{0.1}\text{O}_{10} < \text{Li}_{1.8}\text{La}_2\text{Ti}_{2.8}\text{Nb}_{0.2}\text{O}_{10} < \text{Li}_{1.75}\text{La}_2\text{Ti}_{2.75}\text{Nb}_{0.25}\text{O}_{10}$

**Figure 5.5:** Impedance fits for all materials: (a) $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$. (b) Li-deficient compounds $\text{Li}_{1.9}\text{La}_2\text{Ti}_{2.9}\text{Nb}_{0.1}\text{O}_{10}$, $\text{Li}_{1.8}\text{La}_2\text{Ti}_{2.8}\text{Nb}_{0.2}\text{O}_{10}$, and $\text{Li}_{1.75}\text{La}_2\text{Ti}_{2.75}\text{Nb}_{0.25}\text{O}_{10}$. (c) La-deficient compounds $\text{Li}_2\text{La}_{1.9}\text{Ti}_{2.7}\text{Nb}_{0.3}\text{O}_{10}$ and $\text{Li}_2\text{La}_{1.8}\text{Ti}_{2.4}\text{Nb}_{0.6}\text{O}_{10}$. (d) Both Li- and La-deficient compound, $\text{Li}_{1.9}\text{La}_{1.9}\text{Ti}_{2.6}\text{Nb}_{0.4}\text{O}_{10}$. 

101
Unlike $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, the lithium-deficient material $\text{Li}_{1.9}\text{La}_2\text{Ti}_{2.9}\text{Nb}_{0.1}\text{O}_{10}$ showed measurable conductivity at temperatures above 100 °C, while $\text{Li}_{1.8}\text{La}_2\text{Ti}_{2.8}\text{Nb}_{0.2}\text{O}_{10}$ and $\text{Li}_{1.75}\text{La}_2\text{Ti}_{2.75}\text{Nb}_{0.25}\text{O}_{10}$ showed room temperature conductivity. These results confirm that ionic mobility is facilitated by vacancies in the lithium layer. The conductivity values of the lithium-deficient materials are 2 – 3 orders of magnitude greater than that of $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, as shown in Table 5.3. It is noted that the lithium layer is located in the $ab$ plane (Figure 5.1) in inter-stack spaces, and lithium ions are expected to be mobile through this layer if free hopping sites are available. Therefore, the improvement in lithium-ion conductivity upon the incorporation of defects in this layer was expected.

**Table 5.3:** Variable temperature conductivity of Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity at Different Temperatures (Scm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>$\text{Li}_2\text{La}_2\text{Ti}<em>3\text{O}</em>{10}$</td>
<td>N/A</td>
</tr>
<tr>
<td>$\text{Li}<em>{1.9}\text{La}<em>2\text{Ti}</em>{2.9}\text{Nb}</em>{0.1}\text{O}_{10}$</td>
<td>N/A</td>
</tr>
<tr>
<td>$\text{Li}<em>{1.8}\text{La}<em>2\text{Ti}</em>{2.8}\text{Nb}</em>{0.2}\text{O}_{10}$</td>
<td>7.11 x 10$^{-10}$</td>
</tr>
<tr>
<td>$\text{Li}<em>{1.75}\text{La}<em>2\text{Ti}</em>{2.75}\text{Nb}</em>{0.25}\text{O}_{10}$</td>
<td>4.26 x 10$^{-9}$</td>
</tr>
<tr>
<td>$\text{Li}<em>2\text{La}</em>{1.9}\text{Ti}<em>{2.7}\text{Nb}</em>{0.3}\text{O}_{10}$</td>
<td>6.35 x 10$^{-10}$</td>
</tr>
<tr>
<td>$\text{Li}<em>2\text{La}</em>{1.8}\text{Ti}<em>{2.6}\text{Nb}</em>{0.6}\text{O}_{10}$</td>
<td>2.92 x 10$^{-9}$</td>
</tr>
<tr>
<td>$\text{Li}<em>{1.9}\text{La}</em>{1.9}\text{Ti}<em>{2.6}\text{Nb}</em>{0.4}\text{O}_{10}$</td>
<td>1.69 x 10$^{-8}$</td>
</tr>
</tbody>
</table>
However, we also hypothesized that it may be possible to encourage lithium ions to diffuse in the c-direction (Figure 5.1) by creating defects in the intra-stack A′-sites, where lanthanum is located. We confirmed this hypothesis through the synthesis of a series of La-deficient materials, that showed systematic enhancement of conductivity as a function of La-deficiency:

\[ \text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} < \text{Li}_2\text{La}_{1.90}\text{Ti}_{2.7}\text{Nb}_{0.3}\text{O}_{10} < \text{Li}_2\text{La}_{1.80}\text{Ti}_{2.40}\text{Nb}_{0.60}\text{O}_{10}. \]

The La-deficient compounds demonstrate measurable conductivity and impedance semicircles at room temperature, with conductivities comparable to those observed in lithium-deficient compounds described above.

Given the enhancement of lithium-ion conductivity due to the creation of defects in either A or A′-sites, we postulated that simultaneous incorporation of defects in both sites could enhance the conductivity even further. We, therefore, synthesized Li\(_{1.9}\)La\(_{1.9}\)Ti\(_{2.6}\)Nb\(_{0.4}\)O\(_{10}\), which showed greater conductivity than all of the above materials, reaching \(\sim 10^{-3}\) S cm\(^{-1}\) at 400 °C, as shown in Table 3. This is an important new finding, which indicates that the cooperative effect of defects on both inter- and intra-stack sites has a significantly greater impact on enhancing the lithium-ion conductivity than the defects in any of those sites alone. It is important to note that Li\(_{1.9}\)La\(_{1.9}\)Ti\(_{2.6}\)Nb\(_{0.4}\)O\(_{10}\) shows higher lithium-ion conductivity, even though the total degree of cation-deficiency on both A or A′-sites in this material is the same or smaller than that in compounds containing defects on only one of the two sites. For example, Li\(_2\)La\(_{1.80}\)Ti\(_{2.40}\)Nb\(_{0.60}\)O\(_{10}\) has the same level of overall cation-deficiency as Li\(_{1.9}\)La\(_{1.9}\)Ti\(_{2.6}\)Nb\(_{0.4}\)O\(_{10}\), but the latter features much greater conductivity. On the other hand, Li\(_{1.75}\)La\(_2\)Ti\(_{2.75}\)Nb\(_{0.25}\)O\(_{10}\) has a larger overall cation-deficiency than
Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$, but the latter shows higher conductivity. This indicates the importance of the cooperative effect of both A and A'-sites on lithium-ion conductivity. The impedance spectroscopy data for each material can be used to determine the contributions from different components of resistance using models that consist of different equivalent circuits. For example, the semicircle in the Nyquist plot of Li$_2$La$_2$Ti$_3$O$_{10}$ at 200 °C was fitted using three resistance-capacitance (RC) elements in series (Figure 5.5). This model, comprising three RC units, is often found for perovskite-type ionic conductors. The first and second RC units describe the merging of two relaxation processes with similar time scales, corresponding to the bulk and grain boundary contributions to total conductivity. Whereas the third RC unit is attributed to electrode interface interactions. Impedance spectra for the other materials, namely lithium and lanthanum-deficient compounds, can be fitted with the same electrical model at lower temperatures. For these materials, at 100 °C and above, the semicircles gradually shrink and can be fitted with two resistance-capacitance (RC) units in series. The RC units used in all models are followed by a constant-phase-element (CPE) on the far right, which models the low-frequency tail arising from the blocking nature of the electrode.

The measured conductivities exhibited Arrhenius behavior. The activation energy for the temperature-dependent increase in conductivity in these materials was calculated based on the Arrhenius equation for thermally activated processes:

$$\log T = \log \sigma_0 - \left( \frac{E_a}{2.303kT} \right)$$

where $\sigma_0$ is a pre-exponential factor, characteristic of the material, and $E_a$, $k$, and $T$ are the activation energy, Boltzmann constant, and the absolute temperature, respectively. Arrhenius plots showing the temperature dependence of conductivity in all materials are
presented in Figure 5.6. The calculated $E_a$ for Li$_2$La$_2$Ti$_3$O$_{10}$ was 0.812 eV, while those of lithium-deficient compounds were 0.724 eV for Li$_{1.9}$La$_2$Ti$_{2.9}$Nb$_{0.1}$O$_{10}$, 0.638 eV for Li$_{1.8}$La$_2$Ti$_{2.8}$Nb$_{0.2}$O$_{10}$, and 0.594 eV for Li$_{1.75}$La$_2$Ti$_{2.75}$Nb$_{0.25}$O$_{10}$.

Figure 5.6: Arrhenius plots for all compounds. (a) Plot of Li$_2$La$_2$Ti$_3$O$_{10}$ with all lithium deficient compounds. (b) Plots of Li$_2$La$_2$Ti$_3$O$_{10}$ with all lanthanum deficient and a combination of lithium and lanthanum deficient compounds.

Note the systematic decrease in activation energy as a function of lithium deficiency which trails the increase in conductivity. A similar effect is also observed for the lanthanum-deficient compounds, Li$_2$La$_{1.9}$Ti$_{2.7}$Nb$_{0.3}$O$_{10}$ and Li$_2$La$_{1.8}$Ti$_{2.4}$Nb$_{0.6}$O$_{10}$, which showed activation energies of 0.650 eV and 0.617 eV, respectively. Finally, the lowest activation energy is observed for the material with cation deficiency in both lithium and lanthanum sites, Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$, which shows $E_a = 0.555$ eV. This is also the material with the highest conductivity.
5.5 FREQUENCY-DEPENDENT IMPEDANCE AND DIELECTRIC ANALYSES

The complex electrochemical impedance can be calculated from the equation: $Z^* = Z' - jZ''$, where $Z'$ and $Z''$ are the real and imaginary axes of the plot respectively. These two components can be described as:\textsuperscript{121}

$$Z' = \frac{R_g}{1+(\omega R_g C_g)^2} + \frac{R_{gb}}{1+(\omega R_{gb} C_{gb})^2}$$

$$Z'' = \frac{R_g}{1+(\omega R_g C_g)^2} + \frac{R_{gb}}{1+(\omega R_{gb} C_{gb})^2}$$

where $\omega =$ angular frequency, $R_g =$ grain resistance, $R_{gb} =$ grain boundary resistance, $C_g =$ grain capacitance, and $C_{gb} =$ grain boundary capacitance. Detailed analyses of the real and imaginary components of impedance further highlight the effect of cation deficiency on the mobility of lithium ions. Representative plots of these analyses are shown in Figures 5.7, where the least and most conductive materials, namely Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$, are compared. Figures 5.7a show the variation of the real component of impedance ($Z'$) with angular frequency at different temperatures. From these plots, it is observed that the magnitude of $Z'$ decreases with a rise in temperature in the low-frequency region and seems to merge in the high-frequency region. This behavior is frequently observed in materials of this class,\textsuperscript{121, 125-128} owing to the depression of energy barriers,\textsuperscript{127} which lead to the improvement of conductivity across grain-boundaries.\textsuperscript{125-127} The decrease in $Z'$ with temperature is consistent with the negative temperature coefficient of resistance in these materials,\textsuperscript{125-127}

The variation of the imaginary component of impedance ($Z''$) as a function of angular frequency at different temperatures is also shown in Figures 5.7b. A broad peak, which is a common feature of $Z''$ vs angular frequency plots,\textsuperscript{121, 125-127} is observed. This peak specifies the existence of immobile species at low temperatures. At higher temperatures, the peak gradually levels and shifts towards higher frequency, indicating that
the immobile species become mobile at a higher temperature. The decrease in the magnitude of $Z''$ with temperature further confirms the temperature dependence of relaxation phenomena within these materials.\textsuperscript{125-127} Similarly, the peak shift toward higher frequencies implies an increase in ion-hopping rates.\textsuperscript{121} The effect of cation deficiency is clearly demonstrated in Figures 5.7b. For Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$, the peak only appears at low temperature and disappears at 200 °C. Whereas for Li$_2$La$_3$Ti$_3$O$_{10}$, the $Z''$ peak is present at 200 °C (and at a lower frequency than the cation-deficient compound’s peak) and persists at temperatures up to 400 °C. These observations indicate the significantly greater mobility of lithium ions in Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$, consistent with its considerably higher conductivity.

We also analyzed the variation of dielectric constant ($\varepsilon'$) and loss tangent ($\tan \delta$) as a function of angular frequency at different temperatures. These parameters are expressed using the following equations:

$$
\varepsilon' = \frac{t}{\omega \varepsilon_0 Z'} \frac{-Z}{Z'^2 + Z''^2}, \quad \varepsilon'' = \frac{t}{\omega \varepsilon_0 Z'} \frac{Z'}{Z'^2 + Z''^2}, \quad \tan \delta = \frac{\varepsilon''}{\varepsilon'},
$$

where $A$, $t$, $\varepsilon_0$, $Z'$ and $Z''$ represent the cross-sectional area, thickness, permittivity of free space, the real and imaginary components of impedance, respectively.\textsuperscript{121, 129, 130} Minor variations of these equations are observed in the literature, where $t/A\varepsilon_0$ is represented as the inverse of capacitance $1/C_0$,\textsuperscript{46, 47} and the negative sign in the numerator is sometimes absent.\textsuperscript{46, 47}

The dielectric constant is typically attributed to the dipolar, electronic, ionic, or interfacial polarization effects.\textsuperscript{126} Figure 5.8a shows representative dielectric constant vs frequency plots, where the least and most conductive materials, namely Li$_2$La$_3$Ti$_3$O$_{10}$ and
Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$, are compared. The high magnitude of dielectric constant at lower frequencies is related to dipolar and interfacial polarization within the material, i.e., the so-called Maxwell–Wagner–Sillar polarization. At higher frequencies, electric dipoles cannot adapt to the fast reversal of the AC electric field, and dielectric properties arise primarily from electronic polarization. The decrease in dielectric constant at a higher frequency is typical behavior of ionic conductors, and indicates the negligible contribution from electronic polarization. The magnitude of dielectric constant increases as a function of temperature, due to the increase in the mobility of charge-carriers and more facile reorientation of dipoles at higher temperatures. As a result, the plateau in the dielectric plot also shifts toward a higher frequency.
Figure 5.7: (a) Variation of real components of impedance as a function of frequency ($Z'$ vs log $\omega$) of Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.8}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. (b) Variation of the imaginary component of impedance as a function of frequency ($Z''$ vs log $\omega$) of Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$
As shown in Figure 5.8a, there is a significant difference between the dielectric constants of Li$_2$La$_2$Ti$_3$O$_{10}$ and Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$. The dielectric magnitude is significantly higher in the latter material and persists through a much higher frequency range before reaching a plateau. This is expected given the higher mobility of ions in the latter material. Figure 5.8b shows the plots of loss tangent (tan δ) as a function of angular frequency. The dielectric loss arises from the dissipation of the electrical energy that would otherwise be used to induce polarization within the material.\(^{121}\) As commonly observed in ionic conductors, the plot of tan δ versus frequency shows a broad peak.\(^{20}\) The peak shifts to a higher frequency as temperature increases, representing the improvement in the mobility of charge-carrier species.\(^{20,128}\) As observed in Figure 7b the loss tangent peaks are shifted significantly toward the high-frequency region for the highly conductive material Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$, as compared with Li$_2$La$_2$Ti$_3$O$_{10}$. This observation once again confirms the enhanced mobility of lithium ions in the former compound, consistent with its higher conductivity.
Figure 5.8: (a) Variation of dielectric constant as a function of frequency of $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ and $\text{Li}_{1.9}\text{La}_{1.9}\text{Ti}_{2.6}\text{Nb}_{0.4}\text{O}_{10}$. (b) Variation tangent loss as a function of frequency of $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ and $\text{Li}_{1.9}\text{La}_{1.9}\text{Ti}_{2.6}\text{Nb}_{0.4}\text{O}_{10}$.

5.6 CONCLUSIONS

The lithium-ion conductivity in triple-layered ($n = 3$) Ruddlesden-Popper oxides can be enhanced by inducing cation deficiency in either inter-stack or intra-stack sites. However, a more significant enhancement in ionic conductivity can be achieved through the cooperative effect of both inter- and intra-stack positions. A material with cation deficiency on both sites shows significantly higher ionic conductivity than materials with deficiency on only one site. This is true even if the total degree of cation-deficiency on both inter- and intra-stack sites is the same or smaller than that in compounds containing
defects on only one of the two sites. The systematic studies presented here reveal the pathways through which the ion-hopping takes place and reveals the structural parameters that can be manipulated to enhance the ionic conductivity of triple-layered Ruddlesden-Popper oxides.
CHAPTER 6

LITHIUM-ION MOBILITY IN LAYERED OXIDES Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$
AND Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$, ENHANCED BY SUPERCELL FORMATION

6.1 EXPERIMENTAL

The synthesis and structural elucidation by powder X-ray, neutron diffraction experiments, and ionic conductivity measurements (~1.20 mm in thickness and 5.5 mm in diameter) were performed analogous to the procedure presented in Chapter 2 above. Pure samples were obtained by heating the pelletized samples twice at 1150 °C for 6 hours with one intermittent grinding. Lithium loss due to evaporation at high temperature was compensated for by adding 10% extra Li$_2$CO$_3$, at the start of each synthesis.

The work described in this chapter was published in the Journal of Energy Chemistry, 2021, 60, 75.
6.2 RESULTS AND DISCUSSION

6.3 CRYSTAL STRUCTURE

The only information available on any of these materials is a report on the structure of Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, studied by powder X-ray diffraction, suggesting a tetragonal $I4/mmm$ structure. However, given the dependence of the X-ray form factor on atomic number, the limitations of laboratory X-ray diffraction in the study of materials containing light atoms such as oxygen and in particular lithium should be noted.

Figure 6.1: (a) Crystal structure of a three-layer Ruddlesden-Popper oxide, $A_2A'B_3O_{10}$, where BO$_6$ octahedra are shown in green, intra-stack A-cations as blue spheres, and inter-stack A'-cations as small purple spheres. (b) Coordination geometry and connectivity of lithium ions.
We, therefore, combined X-ray with neutron diffraction to accurately determine the structures of these materials. The diffraction patterns of all three compounds can be readily indexed on a tetragonal cell. Given that, compared with X-ray, the neutron diffraction data are considerably more sensitive to lithium, it was possible to observe that some peaks for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$ could not be modeled using $I4/mmm$ (# 139) as shown in Figure 6.2. However, a slight lowering of the symmetry to $P4_2/nmc$ (# 138) leads to an excellent match. This is the space group previously used for another triple-layered Ruddlesden-Popper oxide, Li$_2$La$_{1.78}$(Nb$_{0.66}$Ti$_{2.34}$)O$_{10}$.	extsuperscript{91} This model has a supercell that is $\sqrt{2}a \times \sqrt{2}b \times 1c$ larger than the $I4/mmm$ unit cell and distributes lithium-ions over two sites (3/4, 1/4, 1/4) and (3/4, 3/4, z). The Sr-analogue, Li$_2$Sr$_{1.5}$Nb$_3$O$_{10}$, has an $I4/mmm$ structure with typical Ruddlesden-Popper unit cell in the long range, although the formation of a larger cell in local domains has been suggested.	extsuperscript{65} On the contrary, our Ca-containing compound features long-range structural distortion, which leads to the transformation of the space group and supercell formation in the entire lattice. The same structure and space group, tetragonal $P4_2/nmc$, is also observed in the other two materials Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. Figure 6.3 shows the refinement profile for all three compounds. Neutron diffraction experiments were performed for the two materials at the two ends of the series, namely the compound containing no tantalum, Li$_2$Ca$_{1.5}$NbTa$_2$O$_{10}$, and the one with two tantalum atoms, Li$_2$Ca$_{1.5}$NbTa$_2$O$_{10}$. The refined structural parameters for these compounds are listed in Tables 6.1 and 6.2. It is noted that introducing three tantalum atoms into the structure would consistently lead to the formation of multi-phase products. Note that while Nb(V) and Ta(V) have similar ionic radii, differences in Ruddlesden-Popper oxides containing these two ions have been reported,\textsuperscript{107} where the Nb-containing materials
show a higher degree of octahedral distortion than the Ta-compounds. This has been explained by the difference in the HOMO-LUMO gap of $d^0$ cations, which controls the off-center distortion of octahedra. This gap is larger for heavier ions, e.g., Ta(V), resulting in less distortion. This could also be described in terms of polarization by hard/soft ions.

Figure 6.2: Comparison between neutron diffraction refinements with $I4/mmm$ and $P4_2/nca$ for $Li_2Ca_{1.5}Nb_3O_{10}$. Stars mark the peaks that do not match $I4/mmm$. 
Table 6.1: Refined structural parameters from powder neutron diffraction data for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$. Space group $P4_2/nmc$, $a = 5.49014(21)$ Å, $c = 26.2456(14)$ Å, $R_p = 0.0997$, $R_{wp} = 0.1197$

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<th>$z$</th>
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<th>$U_{iso}$</th>
<th>Multiplicity</th>
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Table 6.2: Refined structural parameters from powder neutron diffraction for Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. Space group $P4_2/nmc$, $a = 5.49393(19)$ Å, $c = 26.1661(13)$ Å, $R_p = 0.0974$, $R_{wp} = 0.1051$

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Figure 6.3: (a) Rietveld refinements with powder X-ray diffraction for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$ in P4$_2$/nmc. (b) Rietveld refinements with neutron diffraction data for the two end members of the series, Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$ in P4$_2$/nmc. The experimental data, the model, Bragg peak positions, and the difference plot are represented by black crosses, red lines, vertical tick marks, and the lower blue line, respectively.

The three compounds, Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$, and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$ contain corner-sharing (Nb/Ta)O$_6$ octahedra that form triple-layered stacks along the z-direction (Figure 6.1), resulting in the c-axis of the unit cell to be significantly longer than a and b. Given the very long axis, c = 26.2626(3) Å, relative to a = b = 5.4924(0) Å, preferential orientation in the hkl 00l plane was taken into consideration in Rietveld refinements. In this case, March-Dollase formalism was used, which has been previously utilized in Rietveld’s refinement of Ruddlesden-popper phases. As shown in Figure 6.1,
the triple-layered stacks in these materials are separated by lithium ions. Within each stack, the two outer layers of octahedra show a significantly greater degree of distortion than the layer in the middle.\textsuperscript{135} The lithium ions are located at inter-stack spaces and form LiO\textsubscript{4} tetrahedra. The structural distortion that results in the \textit{P42/nmc} supercell also leads to two types of LiO\textsubscript{4} units, i.e., a regular tetrahedron where all Li-O bonds are identical, and a distorted tetrahedron with two different types of Li-O bonds. These LiO\textsubscript{4} units are connected through edge-sharing, resulting in a 2-dimensional network, as shown in Figure 6.1. The calcium atoms are located in spaces between the octahedra in intra-stack sites. However, given the calcium stoichiometry in the formula, only 75\% of intra-stack sites are occupied, and the rest are empty.

Scanning electron microscopy (SEM) was also done to examine the microstructure of these compounds. There is a systematic change in the microstructure of the three compounds, as observed in Figure 6.4. The crystallite size gradually decreases in progression from Li\textsubscript{2}Ca\textsubscript{1.5}Nb\textsubscript{3}O\textsubscript{10} to Li\textsubscript{2}Ca\textsubscript{1.5}TaNb\textsubscript{2}O\textsubscript{10} and Li\textsubscript{2}Ca\textsubscript{1.5}Ta\textsubscript{2}NbO\textsubscript{10}.
Figure 6.4: Scanning electron microscopy images showing the microstructures (a) Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, (b) Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and (c) Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

6.4 IONIC CONDUCTIVITY

All three materials were studied by electrochemical impedance spectroscopy (EIS), over the temperature range 25 to 400 °C. The impedance measurements of Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$, and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$ at room temperature showed a depressed semicircle in the high-to-intermediate frequency range followed by a spike (straight line) at low frequency. The observed semicircle is related to the migration of Li$^+$ ions in the grain interior and across the grain boundaries, and the appearance of the low-frequency spike is attributed to Li$^+$ blocking by gold electrodes. The intercept of the semicircle with the real axis of the Nyquist plot ($Z'$) indicates the total resistance of each
material. The resistance is then used to obtain the total conductivity (grain and grain boundary) using the equation:

$$\sigma = \frac{L}{RA}$$

Here $\sigma$, $L$, $R$, and $A$ represent the total conductivity, thickness of the cylindrical pellet, resistance, and cross-sectional surface area of the pellet, respectively.

Figure 6.5 presents typical Nyquist plots of electrochemical impedance spectra for $\text{Li}_2\text{Ca}_{1.5}\text{Nb}_3\text{O}_{10}$, $\text{Li}_2\text{Ca}_{1.5}\text{Ta}\text{Nb}_2\text{O}_{10}$ and $\text{Li}_2\text{Ca}_{1.5}\text{Ta}_2\text{NbO}_{10}$, at 25 °C and 100 °C. The Sr-analogue, $\text{Li}_2\text{Sr}_{1.5}\text{Nb}_3\text{O}_{10}$, has been reported to lack measurable ionic conductivity at temperatures below 375 °C.\textsuperscript{65} Even at that temperature, the conductivity of the Sr-analogue\textsuperscript{65} is about two orders of magnitude lower than our compounds. The lack of measurable conductivity at room temperature has also been observed in a number of bilayers Ruddlesden-Popper materials such as $\text{Li}_2\text{Sr}\text{Ta}_2\text{O}_7$, $\text{Li}_2\text{Sr}\text{Nb}_2\text{O}_7$, and $\text{Li}_2\text{La}\text{TaTiO}_7$.\textsuperscript{43, 82} We note that the supercell formation in our Ca-containing compounds results in a long-range change in lithium coordination environment (i.e., two types of LiO\textsubscript{4} tetrahedra, one regular and one irregular) compared with the Sr-analogue (only regular tetrahedra). This difference in the lithium coordination can be responsible for the enhanced lithium-ion conductivity in our compounds. The presence of lithium ions in two coordination environments, in particular the irregular LiO\textsubscript{4} coordination geometry, appears to make them less stationary in their position, thus increasing their mobility.
Figure 6.5: Typical impedance fits for (a) Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, (b) Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and (c) Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$, at 25 and 100 °C.

In this series, Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$ exhibits the highest conductivity. As shown in Table 3, a systematic trend is observed, indicating the following order of conductivity:

$$\text{Li}_2\text{Ca}_{1.5}\text{Nb}_3\text{O}_{10} < \text{Li}_2\text{Ca}_{1.5}\text{TaNb}_2\text{O}_{10} < \text{Li}_2\text{Ca}_{1.5}\text{Ta}_2\text{NbO}_{10}$$

The difference in conductivity in this series is significant up to 300 °C. Above this temperature the conductivity values are not significantly different, 7.33 × 10$^{-3}$, 3.18 × 10$^{-3}$ and 2.42 × 10$^{-3}$ S cm$^{-1}$, for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$, and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$, respectively, at 400 °C. All observed semicircles of the impedance data in the Nyquist plot showed a non-Debye response, typical of ionic conductors. The data are interpreted through the fitting of impedance plots with Randles equivalent circuits using a combination of resistance-capacitance (RC) elements and constant phase elements (CPE). These fits give insight into contributions from bulk and grain boundary to the total conductivity of each material. For the materials studied in this work, RC elements describe the integration of two or three relaxation processes with nearly identical time scales occurring in the
material. At room temperature, the data for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$, and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$ could be fitted using a model consisting of three resistance-capacitance (RC) elements, as represented in the inset of Figure 6.5. The first RC unit corresponds to the bulk and the second to grain boundary contribution to the total resistance. The third RC element originates from electrode-sample interface reactions as also observed in other ionic conductors, such as well-known lithium lanthanum titanate perovskite. As temperature increases, the semicircles shrink. The data at 100 °C can be fitted by two RC elements where conductivity contributions originate from the bulk and the grain boundary. These relaxations are immediately followed by a possible diffusion of ions in the samples as demonstrated by the Warburg element ($W_0$). At temperatures above 100 °C, the semicircle diminishes steadily, making it difficult to distinguish the contributions from bulk and grain boundary at high temperature. This is a feature that is common in ionic conductors such as perovskite and garnet-type oxides.

Table 6.3: Variable-temperature conductivity of Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Total Conductivities of Materials, $\sigma$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>Li$<em>2$Ca$</em>{1.5}$Nb$<em>3$O$</em>{10}$</td>
<td>5.09 × 10$^{-8}$</td>
</tr>
<tr>
<td>Li$<em>2$Ca$</em>{1.5}$TaNb$<em>2$O$</em>{10}$</td>
<td>5.87 × 10$^{-9}$</td>
</tr>
<tr>
<td>Li$<em>2$Ca$</em>{1.5}$Ta$<em>2$NbO$</em>{10}$</td>
<td>1.73 × 10$^{-9}$</td>
</tr>
</tbody>
</table>

The activation energies for the thermal dependence of conductivity in these materials can be estimated using the Arrhenius equation for thermally activated conductivity: 

$$\sigma T = \sigma_0 e^{-\frac{E_a}{kT}}$$
Here $\sigma$, $E_a$, $k$, and $T$ represent the pre-exponential factor, which is a material characteristic, the activation energy, Boltzmann constant, and the absolute temperature, respectively. The Arrhenius plots for all compounds are shown in Figure 6.6. As observed, here the activation energies of these compounds vary systematically from 0.587 to 0.650 and 0.691 eV for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$, respectively. This trend follows the conductivity of these materials, where the most conductive compound, Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, shows the lowest activation energy. In addition, all three materials show excellent thermal stability and air stability. X-ray diffraction data for these materials before and after heating to 800 °C are shown in Figure 6.7.

**Figure 6.6:** Arrhenius plots Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. 
Figure 6.7: X-ray diffraction data before and after heating to 800 °C in air, indicating excellent stability.

6.5 FREQUENCY-DEPENDENT IMPEDANCE, DIELECTRIC AND COMPLEX MODULUS ANALYSES

The frequency dependence of different components of impedance (real and imaginary) is presented in Figure 6.8. The plots show a decrease in the real part of impedance, $Z'$, with temperature. However, data from different temperatures merge at high frequency. This gradual temperature-dependent decrease of $Z'$ is due to the decline of energy barriers,\textsuperscript{127} a typical occurrence in materials of this class.\textsuperscript{121,125-128} This is associated
with the enhancement of conductivity across grain-boundaries,\textsuperscript{125-127} and is consistent with the observed negative temperature coefficient of resistance.\textsuperscript{125-127}

The plots of the imaginary component ($Z''$) vs angular frequency in Figure 6.8 show a broad peak whose intensity changes systematically. The lower intensity of the peak in more conductive materials in this series suggests the presence of smaller numbers of non-migratory charged species.\textsuperscript{121, 125-127} In all materials, this broad peak diminishes at higher temperatures. This observation further signifies a weak relaxation at low temperatures, confirming the temperature dependence of relaxation processes in these compounds.\textsuperscript{125-127}, \textsuperscript{144} Furthermore, the peak appears at a higher angular frequency region for more conductive compounds, indicating greater mobility of immobile species and higher ion-hopping rates\textsuperscript{121} in the following order: $\text{Li}_2\text{Ca}{}_{1.5}\text{Ta}_2\text{NbO}_{10}$ $< \text{Li}_2\text{Ca}{}_{1.5}\text{TaNb}_2\text{O}_{10}$ $< \text{Li}_2\text{Ca}{}_{1.5}\text{Nb}_3\text{O}_{10}$.

![Figure 6.8: Variation of real ($Z'$) and imaginary ($Z''$) components of impedance as a function of angular frequency in (a) Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, (b) Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and (c) Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.](image-url)
Figure 6.9: Variation of dielectric constant ($\varepsilon'$) and loss tangent (tan $\delta$) as a function of angular frequency in Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$.

Figure 6.9 shows the variations of dielectric constant ($\varepsilon'$) and loss tangent (tan $\delta$) with respect to the angular frequency at different temperatures for all three materials. The observed polarization can be a result of different processes, such as ionic, dipolar, interfacial, or electronic polarization. The data show characteristically high dielectric constants at lower frequencies, where interfacial and dipolar polarization, also called Maxwell–Wagner–Sillar polarization, are dominant. The dielectric constants decrease steadily to almost zero as a function of frequency owing to the non-compliance of electric
dipoles with the fast variation of the external field at higher frequencies.\textsuperscript{121} This behavior is characteristic of ionic conductors,\textsuperscript{20} indicative of the minimal contribution of electronic polarizations,\textsuperscript{20, 126} which are responsible for any observed dielectric properties at high frequencies.\textsuperscript{20, 126}

It is further observed from Figure 6.9 that the dielectric constant is small at lower temperatures, a feature called nearly constant loss (NCL),\textsuperscript{144} which is attributed to a largely restricted mobility of charge carriers as opposed to the ion-hopping process that occurs at higher temperatures.\textsuperscript{144} The increase in the magnitude of the dielectric constant as a function of temperature is a result of the enhanced mobility of ions\textsuperscript{20} and dipole reorientation.\textsuperscript{121} As observed in Figure 6.9, the most conductive material Li\textsubscript{2}Ca\textsubscript{1.5}Nb\textsubscript{3}O\textsubscript{10} shows significantly higher dielectric constants than the less conductive Li\textsubscript{2}Ca\textsubscript{1.5}TaNb\textsubscript{2}O\textsubscript{10} and Li\textsubscript{2}Ca\textsubscript{1.5}Ta\textsubscript{2}NbO\textsubscript{10}, consistent with higher mobility of ions in more conductive materials.

Figure 6.9 also shows the dielectric loss (\(\tan \delta\)), which is a consequence of the dissipation of the electrical energy, that could have contributed to the instigation of polarization.\textsuperscript{121} The plot of \(\tan \delta\) vs angular frequency shows broad peaks typical of ionic conductors.\textsuperscript{20} These peaks gradually shift to higher frequencies as temperature increases, demonstrating the improvement in the mobility of charge carriers.\textsuperscript{20, 128} The peaks in the more conductive Li\textsubscript{2}Ca\textsubscript{1.5}Nb\textsubscript{3}O\textsubscript{10} appear at significantly higher frequencies than those of the less conductive compounds, Li\textsubscript{2}Ca\textsubscript{1.5}TaNb\textsubscript{2}O\textsubscript{10} and Li\textsubscript{2}Ca\textsubscript{1.5}Ta\textsubscript{2}NbO\textsubscript{10}. This again confirms the greater mobility of lithium ions in Li\textsubscript{2}Ca\textsubscript{1.5}TaNb\textsubscript{2}O\textsubscript{10}.

Figure 6.10 shows the complex modulus spectra for all three materials, Li\textsubscript{2}Ca\textsubscript{1.5}Nb\textsubscript{3}O\textsubscript{10}, Li\textsubscript{2}Ca\textsubscript{1.5}TaNb\textsubscript{2}O\textsubscript{10} and Li\textsubscript{2}Ca\textsubscript{1.5}Ta\textsubscript{2}NbO\textsubscript{10}. The modulus analyses focused
on temperatures up to 300 °C, since at higher temperatures only a spike (tail) is observed in the impedance data. The plots of the real (M’) vs. imaginary (M’”) component of the complex modulus show complete semicircles at lower temperatures, which gradually shrinks into an arc as temperature increases, indicating a temperature-dependent ion hopping in these compounds.\textsuperscript{126}

![Graphs showing complex modulus for different compounds](image)

**Figure 6.10:** Complex modulus for (a) Li\textsubscript{2}Ca\textsubscript{1.5}Nb\textsubscript{3}O\textsubscript{10}, (b) Li\textsubscript{2}Ca\textsubscript{1.5}TaNb\textsubscript{2}O\textsubscript{10} and (c) Li\textsubscript{2}Ca\textsubscript{1.5}Ta\textsubscript{2}NbO\textsubscript{10}.

The plots of M’ vs. angular frequency are also presented in **Figure 6.10**. They show very low M’ value at low frequencies, and an increase in M’ at a higher frequency, often
ascribed to short-range mobility of ions.\textsuperscript{126,128} Subsequently, M' levels at a constant value at higher frequencies suggesting a relaxation taking place within the materials. The M' dispersion frequency follows the same trend as conductivity. The dispersion occurs at a higher frequency for Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$ compared with Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. The plots of the imaginary component of modulus (M’’’) vs. angular frequency are also shown in \textbf{Figure 6.10}. The plots feature peaks that shift to a higher frequency as a function of temperature, indicating the temperature dependence of ionic mobility.\textsuperscript{121,128} The position of the peak indicates the frequency where long-range ionic motion (below the peak) converts into short-range mobility (above the peak).\textsuperscript{126} The asymmetric peaks indicate that relaxations within these materials are non-Debye type, where there are different time constants for the relaxations.\textsuperscript{121,126} The positions of M’’’ peaks show the same trend as conductivity values obtained from impedance spectroscopy, indicating greater mobility of ions in more conductive materials.

6.6 CONCLUSIONS

The lithium-ion conductivity in layered oxides related to the Ruddlesden-Popper structure is affected by distortions that lead to a supercell formation. This is demonstrated through the synthesis and investigation of Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$, Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$, and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. Neutron and X-ray diffraction shows that all three materials crystallize in a tetragonal structure with a supercell that is twice larger than that of typical Ruddlesden-Popper oxides, resulting in the enhancement of their ionic conductivity. A systematic increase in conductivity was observed in this series, where Li$_2$Ca$_{1.5}$Nb$_3$O$_{10}$ has the highest conductivity, followed by Li$_2$Ca$_{1.5}$TaNb$_2$O$_{10}$ and Li$_2$Ca$_{1.5}$Ta$_2$NbO$_{10}$. A similar trend was
observed for the activation energy for a temperature-dependent increase in conductivity. Dielectric and complex modulus analyses further confirmed that the mobility of ions within these materials follows the same trends as the ionic conductivity.
CHAPTER 7

SYMMETRY EFFECT ON THE ENHANCEMENT OF LITHIUM-ION MOBILITY IN LAYERED OXIDES Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta)

7.1 EXPERIMENTAL

All material synthesis and structural elucidation procedures are similar to the description in Chapter 2 of this work. The heating conditions and the compensation of lithium at higher temperatures are the same as those presented in Chapter 5. X-ray photoelectron spectroscopy (Figure 7.3) was also used to confirm the metal valence states in the most lithium conductive compound, Li$_2$Ca$_2$Ta$_5$TiO$_{10}$.

The work described in this chapter was published in Journal of Physical Chemistry C, 2021, 125, 3689.
Figure 7.1: (a) Crystal structure of Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta). (b) The AO$_{12}$, LiO$_4$ and (Ta/Ti)O$_6$ units are shown in green, purple and blue, respectively.

7.2 RESULTS AND DISCUSSION

7.3 CRYSTAL STRUCTURE

The crystal structures of the synthesized materials were examined by X-ray and neutron diffraction. Of the 5 materials studied in this work, the structure of Li$_2$La$_2$Ti$_3$O$_{10}$ has been reported.$^{132}$ But no other information about this compound is available. It has a tetragonal structure with $I4/mmm$ space group. This is a common space group for triple-layered ($n = 3$) Ruddlesden-Popper oxides.$^{132, 133-135}$ Rietveld refinements of X-ray diffraction data for Li$_2$La$_2$Ti$_3$O$_{10}$ confirmed the formation of an $I4/mmm$ system, as shown in Figure 7.2 and Table 7.1. However, Li$_2$SrLaTaTi$_2$O$_{10}$, Li$_2$Sr$_2$Ta$_2$TiO$_{10}$, Li$_2$CaLaTaTi$_2$O$_{10}$, and Li$_2$Ca$_2$Ta$_2$TiO$_{10}$ do not form the same type of structure. As evident
from the insets in Figure 7.2, some of the single peaks in \( I4/mmm \) (space group # 139) broaden and split into more peaks.

**Table 7.1**: Structural parameters from Rietveld refinement using powder X-ray diffraction data for \( \text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} \) in \( I4/mmm \). \( R_p = 0.0578 \), \( R_{wp} = 0.0764 \).

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<th>( y )</th>
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<th>( U_{iso}(\text{Å}^2) )</th>
<th>Multiplicity</th>
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<td>0.25</td>
<td>1</td>
<td>0.0250</td>
<td>4</td>
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<td>1</td>
<td>0.0233(18)</td>
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<tr>
<td>Ti2</td>
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<td>0</td>
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<tr>
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<td>0.108(10)</td>
<td>4</td>
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</tbody>
</table>

We, therefore, lowered the symmetry and examined a \( P4_2/nmm \) model (space group # 138), which has been observed for a related compound, \( \text{Li}_2\text{La}_{1.78}\text{Nb}_{0.66}\text{Ti}_{2.34}\text{O}_{10} \).\(^9^1\) As observed in the inset of Figure 7.2, this model nicely describes the bifurcation of the peaks. This structure has a \( \sim \sqrt{2}a \times \sim \sqrt{2}b \times \sim 1c \) supercell, compared with the \( I4/mmm \) system (hence doubling the unit cell volume), and the lithium-ions are statistically distributed over two positions, \( 4b \) (3/4, 1/4, 1/4) and \( 4e \) (3/4, 3/4, \( z \)). In these Rietveld refinements, preferential orientation correction was applied, as commonly used for layered oxides.\(^1^3^5\) A list of atomic positions of this model is provided in Tables 7.2 – 7.5. Table 7.6 shows the unit cell parameters for all compounds. Despite having larger unit cells, \( \text{Li}_2\text{SrLaTaTi}_2\text{O}_{10} \), \( \text{Li}_2\text{Sr}_2\text{Ta}_2\text{TiO}_{10} \), \( \text{Li}_2\text{CaLaTaTi}_2\text{O}_{10} \), and \( \text{Li}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{10} \) have the same type of coordination geometry and polyhedral connectivity as \( \text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} \). All five compounds have the general formula \( \text{Li}_2\text{A}_2\text{B}_2\text{TiO}_{10} \) (\( \text{A} = \text{La},\text{Sr},\text{Ca}; \text{B} = \text{Ti},\text{Ta} \)), where oxygen atoms form a tetrahedral coordination geometry around lithium, as shown in Figure 7.1.
Figure 7.2: (a-e) Rietveld refinement profiles using X-ray diffraction data for Li$_2$La$_2$Ti$_3$O$_{10}$ (I4/mmm), Li$_2$SrLaTaTi$_2$O$_{10}$, Li$_2$SrTa$_2$TiO$_{10}$, Li$_2$CaLaTaTi$_2$O$_{10}$, and Li$_2$Ca$_2$Ta$_2$TiO$_{10}$ (P4$_2$/ncm). (f) Neutron diffraction data for Li$_2$Ca$_2$Ta$_2$TiO$_{10}$. 

135
Table 7.2: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$SrLaTaTi$_2$O$_{10}$. Space group $P4_2/nnc$, $R_p = 0.0896$, $R_{wp} = 0.1237$.

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Table 7.3: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$Sr$_2$Ta$_2$TiO$_{10}$. Space group $P4_2/nnc$, $R_p = 0.0385$, $R_{wp} = 0.0543$.

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<td>O1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.1609(1)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>-0.0457(2)</td>
<td>0.5457(2)</td>
<td>0.2750(5)</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>0.0442(2)</td>
<td>0.0442(2)</td>
<td>0.0831(7)</td>
<td>1</td>
</tr>
<tr>
<td>O4</td>
<td>0.75</td>
<td>0.75</td>
<td>0.2091(1)</td>
<td>1</td>
</tr>
<tr>
<td>O5</td>
<td>0.75</td>
<td>0.25</td>
<td>0.1480(7)</td>
<td>1</td>
</tr>
<tr>
<td>O6</td>
<td>0.167(4)</td>
<td>0.667(4)</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>O7</td>
<td>0.566(5)</td>
<td>-0.066(5)</td>
<td>0.0468(1)</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table 7.4: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$CaLaTaTi$_2$O$_{10}$. Space group $P4_2/ncm$, $R_p = 0.0393$, $R_{wp} = 0.0522$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
<td>0.4971(2)</td>
<td>0.0029(2)</td>
<td>0.07634(2)</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca1</td>
<td>0.4971(2)</td>
<td>0.0029(2)</td>
<td>0.07634(2)</td>
<td>0.5</td>
</tr>
<tr>
<td>Li1</td>
<td>0.750</td>
<td>0.75</td>
<td>0.2650</td>
<td>1</td>
</tr>
<tr>
<td>Li2</td>
<td>0.75</td>
<td>0.25</td>
<td>0.25</td>
<td>1</td>
</tr>
<tr>
<td>Ti1</td>
<td>0.4987(2)</td>
<td>0.4987(2)</td>
<td>0.15618(2)</td>
<td>0.6667</td>
</tr>
<tr>
<td>Ti2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.6667</td>
</tr>
<tr>
<td>Ta1</td>
<td>0.4987(2)</td>
<td>0.4987(2)</td>
<td>0.15618(2)</td>
<td>0.3333</td>
</tr>
<tr>
<td>Ta2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.3333</td>
</tr>
<tr>
<td>O1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.1430(7)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>0.0490(6)</td>
<td>0.4510(6)</td>
<td>0.2837(1)</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>0.0480(7)</td>
<td>0.0480(7)</td>
<td>0.1303(2)</td>
<td>1</td>
</tr>
<tr>
<td>O4</td>
<td>0.75</td>
<td>0.75</td>
<td>0.1450(7)</td>
<td>1</td>
</tr>
<tr>
<td>O5</td>
<td>0.75</td>
<td>0.25</td>
<td>0.1135(1)</td>
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</tr>
<tr>
<td>O6</td>
<td>-0.2520(3)</td>
<td>0.2480(3)</td>
<td>0.0000</td>
<td>0.5</td>
</tr>
<tr>
<td>O7</td>
<td>0.75</td>
<td>0.25</td>
<td>-0.0060(7)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 7.5: Structural parameters from Rietveld refinement using powder X-ray diffraction data for Li$_2$Ca$_2$Ta$_2$TiO$_{10}$ in $P4_2/ncm$. $R_p = 0.0383$, $R_{wp} = 0.554$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca1</td>
<td>0.5218(3)</td>
<td>-0.0218(3)</td>
<td>0.08129(3)</td>
<td>1</td>
<td>0.0280(4)</td>
<td>8</td>
</tr>
<tr>
<td>Li1</td>
<td>0.750</td>
<td>0.75</td>
<td>0.2650</td>
<td>1</td>
<td>0.0250</td>
<td>4</td>
</tr>
<tr>
<td>Li2</td>
<td>0.75</td>
<td>0.25</td>
<td>0.25</td>
<td>1</td>
<td>0.0250</td>
<td>4</td>
</tr>
<tr>
<td>Ti1</td>
<td>0.4936(1)</td>
<td>0.4936(1)</td>
<td>0.15359(6)</td>
<td>0.306(2)</td>
<td>0.0195(9)</td>
<td>8</td>
</tr>
<tr>
<td>Ti2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.372(2)</td>
<td>0.0257(1)</td>
<td>4</td>
</tr>
<tr>
<td>Ta1</td>
<td>0.4946(1)</td>
<td>0.4946(1)</td>
<td>0.15366(6)</td>
<td>0.694(2)</td>
<td>0.0195(9)</td>
<td>8</td>
</tr>
<tr>
<td>Ta2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.628(2)</td>
<td>0.0257(1)</td>
<td>4</td>
</tr>
<tr>
<td>O1</td>
<td>0.25</td>
<td>0.25</td>
<td>0.1468(3)</td>
<td>1</td>
<td>0.0650(4)</td>
<td>4</td>
</tr>
<tr>
<td>O2</td>
<td>0.0370(4)</td>
<td>0.463(4)</td>
<td>0.2759(7)</td>
<td>1</td>
<td>0.0650(4)</td>
<td>8</td>
</tr>
<tr>
<td>O3</td>
<td>-0.0090(6)</td>
<td>-0.0090(6)</td>
<td>0.0674(7)</td>
<td>1</td>
<td>0.0650(4)</td>
<td>8</td>
</tr>
<tr>
<td>O4</td>
<td>0.75</td>
<td>0.75</td>
<td>0.1517(3)</td>
<td>1</td>
<td>0.0650(4)</td>
<td>4</td>
</tr>
<tr>
<td>O5</td>
<td>0.75</td>
<td>0.25</td>
<td>0.1534(2)</td>
<td>1</td>
<td>0.0650(4)</td>
<td>8</td>
</tr>
<tr>
<td>O6</td>
<td>0.234(2)</td>
<td>0.734(2)</td>
<td>0.5</td>
<td>0.0650(4)</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>O7</td>
<td>0.516(1)</td>
<td>-0.016(1)</td>
<td>0.0314(1)</td>
<td>0.5</td>
<td>0.0650(4)</td>
<td>8</td>
</tr>
</tbody>
</table>
Table 7.6: Space group, unit cell parameters, and volumes for all five materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>Unit Cell Parameters (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Li₂La₂Ti₃O₁₀</td>
<td>I4/mmm</td>
<td>3.8436 (1)</td>
<td>3.8436 (1)</td>
</tr>
<tr>
<td>Li₂SrLaTaTi₂O₁₀</td>
<td>P4₂/nmc</td>
<td>5.5045(2)</td>
<td>5.5045(2)</td>
</tr>
<tr>
<td>Li₂Sr₂Ta₂TiO₁₀</td>
<td>P4₂/nmc</td>
<td>5.5629(1)</td>
<td>5.5629(1)</td>
</tr>
<tr>
<td>Li₂CaLaTaTi₂O₁₀</td>
<td>P4₂/nmc</td>
<td>5.4648(2)</td>
<td>5.4648(2)</td>
</tr>
<tr>
<td>Li₂Ca₂Ta₂TiO₁₀</td>
<td>P4₂/nmc</td>
<td>5.4691(1)</td>
<td>5.4691(1)</td>
</tr>
</tbody>
</table>

To confirm the presence of peak shoulders that correspond to \( P4₂/nmc \), we also conducted neutron diffraction experiments for Li₂Ca₂Ta₂TiO₁₀. As shown in Figure 7.2, neutron experiments also confirm the broadening of the peaks and the lowering of the symmetry. The A-site cations, \( \text{La}^{3+}, \text{Sr}^{2+} \) or \( \text{Ca}^{2+} \), are 12-coordinated, while Ti\(^{4+}\) and Ta\(^{5+}\) ions are 6-coordinated, forming triple-layered stacks of \((\text{Ti/Ta})O_6\) octahedra.

The octahedra in the outer layers of these stacks have significantly large distortions than the ones in the middle layer. ¹³⁵ Note the shifting of each stack relative to the next. The \( \text{La}^{3+}, \text{Sr}^{2+} \) or \( \text{Ca}^{2+} \) ions reside in intra-stack spaces, while Li\(^+\) ion occupies the inter-stack sites. While Li₂La₂Ti₃O₁₀ has four equivalent Li–O bonds, the other four compounds have non-equivalent Li–O bonds, leading to distorted tetrahedra. However, in all five compounds, the connectivity of the LiO₄ tetrahedra is the same, i.e., through edge-sharing. As expected, the Sr-containing compounds shave larger unit cell volumes than the Ca-containing materials given the larger ionic radius of Sr\(^{2+}\) compared with Ca\(^{2+}\). Figure 7.3 confirms the oxidation states of Ta\(^{5+}\) and Ti\(^{4+}\) ions in the most lithium conductive compound, Li₂Ca₂Ta₂TiO₁₀. Scanning electron microscopy (SEM) was done on all compounds to examine their microstructure. As seen in Figure 7.4, Li₂La₂Ti₃O₁₀ has the largest grain size, while the Sr-containing materials show smaller grains and more porosity.
Figure 7.3: X-ray photoelectron spectroscopy data for the most conductive material, Li$_2$Ca$_2$Ta$_2$TiO$_{10}$. Binding energies (eV) are consistent with pentavalent tantalum and tetravalent titanium.\textsuperscript{1,2}

Figure 7.4: (a-e) Scanning electron microscopy images showing the microstructures of Li$_2$La$_2$Ti$_3$O$_{10}$, Li$_2$SrLaTaTi$_2$O$_{10}$, Li$_2$Sr$_2$Ta$_2$TiO$_{10}$, Li$_2$CaLaTaTi$_2$O$_{10}$ and Li$_2$Ca$_2$Ta$_2$TiO$_{10}$.
7.4 IONIC CONDUCTIVITY

We examined the ionic conductivity of all five compounds by electrochemical impedance spectroscopy (EIS) which can provide information about the charge transport in bulk, grain boundary, and electrode interface. It can also give information on relaxation frequencies and capacitances. Typical Nyquist plots of impedance spectra measured for all five compounds at 200 °C are presented in Figure 7.5. At low temperatures, the impedance plots consist of a semicircle and a tail, typical of ionic conductors, owing to the hindering of lithium-ion transport by the electrodes. At higher temperatures, the observed semicircles gradually shrink, indicative of the decrease in material resistance and improved ionic mobility.

Total resistance (grain + grain boundary) of each material is obtained from the intercept of the tail in the Nyquist plot with the real axis (Z'), to calculate the conductivity using the relation: \( \sigma = \frac{L}{RA} \), where \( L \) is the thickness of the sample and \( A \) is the cross-sectional area of the sintered pellet. Table 7.7 lists the total conductivity values for all five compounds. As evident from this table, \( \text{Li}_2\text{CaLaTaTi}_2\text{O}_{10} \) and \( \text{Li}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{10} \) show the highest conductivity values in the series. This is a consequence of multiple factors. The most important parameter is the structural transformation from a typical Ruddlesden-Popper structure of \( \text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} \) to a super-structure in the other four compounds. However, this effect can be opposed or reinforced by the impact of Li-Li distances, grain size, and grain contact. The Li-Li distances are 2.72 Å for \( \text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10} \), 2.77 Å for \( \text{Li}_2\text{SrLaTaTi}_2\text{O}_{10} \), 2.80 Å for \( \text{Li}_2\text{Sr}_2\text{Ta}_2\text{TiO}_{10} \), and 2.76 Å for \( \text{Li}_2\text{CaLaTaTi}_2\text{O}_{10} \) and \( \text{Li}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{10} \). These are comparable to the distances observed in some other Ruddlesden-
Popper oxides, such as Li$_2$Sr$_{1.5}$Nb$_3$O$_{10}$ (2.76 Å),$^{65}$ Li$_2$La$_{1.78}$Nb$_{0.66}$Ti$_{2.34}$O$_{10}$ (2.74 Å),$^{44}$ Li$_2$SrTa$_2$O$_7$ (2.80 Å),$^{43,82}$ and Li$_2$LaTaTiO$_7$ (2.75 Å).$^{82}$

The change in symmetry is the main parameter and has a positive effect on ionic mobility. The least conductive material, Li$_2$Sr$_2$Ta$_2$TiO$_{10}$, has long Li-Li distances, a small grain size (Figure 7.4), and insufficient contact between the grains. On the other hand, in the two most conductive materials, Li$_2$CaLaTaTi$_2$O$_{10}$ and Li$_2$Ca$_2$Ta$_2$TiO$_{10}$, the effect of structural change is reinforced, where Li-Li distances are shorter, which facilitates the hopping of lithium ions between different sites. Also, among the two Ca-containing compounds, the most conductive material, Li$_2$Ca$_2$Ta$_2$TiO$_{10}$, shows better contact between its grains, as observed from the SEM image in Figure 7.4.

The Li-ion conductivities of these compounds are lower than those of fast lithium-ion conductors such as garnets (~10$^{-4}$ S cm$^{-1}$ at 25 °C),$^{92}$ anti-perovskite Li$_3$OCl (4.82 × 10$^{-3}$ S cm$^{-1}$ at 250 °C),$^{93}$ Nasicon Na$_3$[Zr$_{2.6}$Ge$_3$]Si$_2$PO$_{12}$ (1.40 × 10$^{-2}$ S cm$^{-1}$ at 150 °C),$^{94}$ perovskite Li$_{0.30}$La$_{0.57}$TiO$_3$ (1.0 × 10$^{-3}$ S cm$^{-1}$ at 25 °C)$^{33}$ and thio-lisicon Li$_{4-x}$Si$_{1-x}$P$_x$S$_4$ (6.40 × 10$^{-4}$ S cm$^{-1}$ at 27 °C).$^{95}$ However, the Li-ion conductivity of the most conductive material in this series, Li$_2$Ca$_2$Ta$_2$TiO$_{10}$, is higher than those of several other Ruddlesden-Popper oxides, such as Li$_2$SrTa$_2$O$_7$ (3.42 × 10$^{-7}$ S cm$^{-1}$ at 300 °C),$^{90}$ Li$_2$SrNb$_2$O$_7$ (2.10 × 10$^{-6}$ S cm$^{-1}$ at 200 °C),$^{90}$ Li$_2$Sr$_{1.5}$Nb$_3$O$_{10}$ (4.90 × 10$^{-6}$ S cm$^{-1}$ at 280 °C),$^{91}$ Li$_2$La$_2$Ti$_3$O$_{10}$ (3.78 × 10$^{-8}$ S cm$^{-1}$ at 200 °C),$^{39}$ and Li$_2$Sr$_{1.5}$Nb$_{2.885}$Fe$_{0.117}$O$_{10}$ (9.60 × 10$^{-5}$ S cm$^{-1}$ at 390 °C)$^{65}$ across all temperatures.
Table 7.7: Variable temperature conductivity of all five materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity at Different Temperatures (Scm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>Li$_2$La$_2$Ti$<em>3$O$</em>{10}$</td>
<td>N/A</td>
</tr>
<tr>
<td>Li$_2$SrLaTaTi$<em>2$O$</em>{10}$</td>
<td>N/A</td>
</tr>
<tr>
<td>Li$_2$SrTa$_2$Ti$<em>4$O$</em>{10}$</td>
<td>N/A</td>
</tr>
<tr>
<td>Li$_2$CaLaTaTi$<em>2$O$</em>{10}$</td>
<td>1.56 × 10$^{-9}$</td>
</tr>
<tr>
<td>Li$_2$Ca$_2$Ta$<em>2$TiO$</em>{10}$</td>
<td>4.63 × 10$^{-10}$</td>
</tr>
</tbody>
</table>

Table 7.8: Representative R-C values from fits to the Nyquist plots at 200 °C. $R_g$, $R_{gb}$ and $R_{ei}$ indicate the resistances from grain, grain boundary, and electrode-sample interphase.

<table>
<thead>
<tr>
<th>Material</th>
<th>Equivalent Circuit Parameters at 200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_b$ (Ω)</td>
</tr>
<tr>
<td>Li$_2$La$_2$Ti$<em>3$O$</em>{10}$</td>
<td>3.75 × 10$^6$</td>
</tr>
<tr>
<td>Li$_2$SrLaTaTi$<em>2$O$</em>{10}$</td>
<td>7.02 × 10$^7$</td>
</tr>
<tr>
<td>Li$_2$SrTa$_2$Ti$<em>4$O$</em>{10}$</td>
<td>1.51 × 10$^8$</td>
</tr>
<tr>
<td>Li$_2$CaLaTaTi$<em>2$O$</em>{10}$</td>
<td>1.30 × 10$^5$</td>
</tr>
<tr>
<td>Li$_2$Ca$_2$Ta$<em>2$TiO$</em>{10}$</td>
<td>3.29 × 10$^4$</td>
</tr>
</tbody>
</table>

*Used for fitting the tail in the Nyquist plot.
The electrochemical impedance data can be modeled using equivalent resistance-capacitance (RC) electrical circuits. Typically, conductivity in polycrystalline materials is dependent on conduction through both the grain and grain boundaries. At lower temperatures, where impedance semicircles are well-defined, the Nyquist plot could be fitted using an electrical model consisting of three RC elements in series and a constant phase element (CPE) for modeling the tail, as presented in the inset of Figure 7.5.

Figure 7.5: Impedance fits for all five materials at 200 °C.
In this model, the first two RC elements describe the integration of two relaxation processes with similar time scales which originate from the grain and grain boundaries.\textsuperscript{81} The third RC element in this electrical model is related to the electrode-sample interface, as observed in some well-known ionic conductors, such as lithium lanthanum titanate perovskite.\textsuperscript{33, 109} At temperatures beyond 200 °C, as the conductivity increase, the semicircles steadily shrink and the data can be fitted with two RC units.

The variation of conductivities with temperature follows the Arrhenius behavior. The thermally activated increase in conductivity can be described based on the following relation:\textsuperscript{82}

\[
\log \sigma T = \log \sigma_o - \left( \frac{E_a}{2.303 kT} \right) \quad (1)
\]

where $\sigma_o$ is a pre-exponential factor, characteristic of the material, and $E_a$, $k$ and $T$ are the activation energy, Boltzmann constant, and the absolute temperature respectively.\textsuperscript{123, 124} The activation energy for temperature-dependent increase in conductivity can be obtained from the slope of the Arrhenius plot, presented in Figure 7.6. The activation energy (Ea) values are 0.850 eV for Li$_2$La$_2$Ti$_3$O$_{10}$, 0.813 eV for Li$_2$SrLaTaTi$_2$O$_{10}$, 0.940 eV for Li$_2$Sr$_2$Ta$_2$TiO$_{10}$, 0.738 eV for Li$_2$CaLaTaTi$_2$O$_{10}$ and 0.693 eV for Li$_2$Ca$_2$Ta$_2$TiO$_{10}$. The latter two compounds, which have the highest conductivities, show the lowest activation energies. These can be compared to the activation energies of some other Ruddlesden-Popper oxides, such as Li$_2$SrTa$_2$O$_7$ (0.78eV),\textsuperscript{43} Li$_2$SrNbTaO$_7$ (0.85eV),\textsuperscript{90} Li$_2$SrNb$_2$O$_7$ (0.64eV),\textsuperscript{90} Li$_2$LaTaTiO$_7$ (0.61eV).\textsuperscript{82} They are also larger than the activation energies for some fast lithium-ion conductors, such as Li$_{3+x}$La$_{2/3-x}$□$_{1/3}$Ta$_2$O$_3$(0.36 eV),\textsuperscript{145} LiTaSiO$_5$ (0.46eV)\textsuperscript{8} and garnets, Li$_{5+2x}$La$_3$Ta$_{2-x}$Y$_x$O$_{12}$ (0.33-0.43 eV).\textsuperscript{18}
Figure 7.6: Arrhenius plots for all five compounds, Li₂A₂B₂TiO₁₀ (A= La, Sr, Ca; B = Ti, Ta).

7.5 FREQUENCY-DEPENDENT IMPEDANCE

Figure 7.7 shows the frequency dependence of real component (Z’) of impedance, $Z’ = Z’ - jZ''$, with angular frequency at different temperatures. A monotonic decrease in $Z’$ is observed with the rise in temperature, which is in agreement with the negative temperature coefficient of resistance in these compounds.¹²⁵-¹²⁷ There is also a decrease in $Z’$ as a function of frequency, and the data for different temperatures merge in the high-frequency region. The frequency-dependent decline in $Z’$ is common in compounds of this class,¹²¹,¹²⁵-¹²⁸ owing to the lowering of energy barriers,¹²⁷ resulting in the conductivity enhancement across grain-boundaries.¹²⁵-¹²⁷ Note that the most conductive compound, Li₂Ca₂Ta₂TiO₁₀, shows the fastest decline in $Z’$ as a function of frequency. The variation of the imaginary component (Z’’) of impedance as a function of angular frequency is shown in Figure 7.8.
The appearance of broad peaks in the plots of Z” vs angular frequency,\textsuperscript{121, 125-127} indicates the presence of immobile charged species at low temperatures,\textsuperscript{127} whose mobility increases as a function of temperature. At higher temperatures, these peaks move to a higher frequency and eventually flatten out. The occurrence of the Z” peak at higher angular frequency signifies a greater hopping rate for localized charge carriers.\textsuperscript{121} The deterioration of the broad peak and also the decrease in Z” value at higher temperatures indicate the dependence of relaxation processes on temperature.\textsuperscript{125-127, 144} The higher mobility of lithium ions in Li$_2$Ca$_2$Ta$_2$TiO$_{10}$ is evident from the Z” plot, where the broad peak disappears at temperatures higher than 100 °C. In contrast, the other materials show the Z” peaks at 200 °C or higher. These observations are consistent with the higher conductivity of Li$_2$Ca$_2$Ta$_2$TiO$_{10}$ compared with other compounds.
Figure 7.7: Variation of the real component of impedance as a function of frequency (Z’ vs logω) for all five compounds, Li₂A₂B₂TiO₁₀ (A= La, Sr, Ca; B = Ti, Ta).
Figure 7.8: Variation of the imaginary component of impedance as a function of frequency ($Z''$ vs log $\omega$) for all five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta).
7.6 DIELECTRIC AND LOSS TANGENT ANALYSES

Figures 7.9 and 7.10 show the frequency-dependent dielectric constant ($\varepsilon'$) and loss tangent (tan $\delta$) at different temperatures. The dielectric constant characteristically is ascribed to the dipolar, electronic, ionic, or interfacial polarization effects. The parameters of dielectric constant ($\varepsilon'$) and loss tangent (tan $\delta$) variation as a function of angular frequency over different temperature ranges are expressed as:

$$\varepsilon' = \frac{t}{\omega A \varepsilon_o} \frac{-Z'}{Z'^2 + Z''^2}, \quad \varepsilon'' = \frac{t}{\omega A \varepsilon_o} \frac{Z'}{Z'^2 + Z''^2}, \quad \tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

where $A$, $t$, $\varepsilon_o$, $Z'$ and $Z''$ represent the cross-sectional area of the sample, the thickness of the sample, permittivity of free space, real component, and imaginary component of impedance, respectively. Figure 7.9 shows that at lower temperatures the dielectric constant value is relatively low and has a weaker dependence on the frequency. This observation which is described as the nearly constant loss (NCL) feature, commonly results from the relaxation of charge carriers migrating in asymmetric double-well potentials. This type of relaxation includes highly localized mobility instead of hopping processes. The dielectric constant in the lower frequency region has a greater magnitude at higher temperatures, where there is an increase in mobility of ions and more facile reorientation of dipoles to align with the field due to higher temperatures.

The dielectric constant steadily decreases with increasing frequency overall temperatures, which is a characteristic behavior of ionic conductors. The low value of the dielectric constant at high frequencies is due to the inability of electric dipoles to adjust to the rapid reversal of the AC electric field. Dielectric properties at lower frequencies are of Maxwell–Wagner–Sillar type, arising from interfacial and dipolar polarization.
Whereas at higher frequencies, the dielectric properties are a result of electronic polarization,\textsuperscript{20,126} and there is little contribution from

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.9.png}
\caption{Variation of dielectric constant ($\varepsilon'$) as a function of frequency for all five compounds, Li$_2$A$_2$B$_2$TiO$_{10}$ (A= La, Sr, Ca; B = Ti, Ta).}
\end{figure}
oscillating charge carriers. The temperature dependence of dipolar polarization is also clear from the shift of the plateau in the dielectric constant to higher frequencies as temperature increases.\textsuperscript{20}

\textbf{Figure 7.10:} Variation of tangent loss ($\tan \delta$) as a function of frequency for all five compounds, $\text{Li}_2\text{A}_2\text{B}_2\text{TiO}_{10}$ (A = La, Sr, Ca; B = Ti, Ta).
The effect of the greater ionic conductivity of Li$_2$CaTa$_2$TiO$_{10}$ is evident from the dielectric plateau, which occurs at a higher frequency compared with other materials, indicating the enhanced mobility of ions in this compound. The plots of dielectric loss as a function of angular frequency are shown in Figures 7.9 and S7.5. Dielectric loss is observed because the electrical energy, that could have resulted in polarization in the material, dissipates.$^{121}$ As typically observed in ionic conductors,$^{20}$ the plot of tan δ as a function frequency features broad peaks, seen in Figure 7.9 and S7.5. At higher temperatures, as the mobility of charge carriers increases, the peak gradually moves to a higher frequency.$^{20, 128}$ A observed from the plots, the peaks for the most conductive material, Li$_2$CaTa$_2$TiO$_{10}$, shift to significantly higher frequencies as compared with the other compounds. This further confirms the enhanced ionic mobility in this compound.

7.7 COMPLEX MODULUS ANALYSIS

The complex modulus studies give insight into the dynamic aspects of the transport process such as rates of ion hopping and relaxation times.$^{121, 126, 128, 140}$ Figure 10 and S6 show the impedance data plotted in the modulus formalism. The complex modulus function for the ion transport can be expressed by the following formalism:$^{121}$

\[
M^* = M' + jM'', \quad M' = \frac{\varepsilon'}{\varepsilon' + \varepsilon''} \quad \text{and} \quad M'' = \frac{\varepsilon''}{\varepsilon' + \varepsilon''},
\]

where the real and imaginary components of the complex modulus, are represented by $M'$ and $M''$, respectively. Also, the real and imaginary parts of dielectric permittivity are shown as $\varepsilon'$ and $\varepsilon''$, respectively.$^{121}$ The first set of graphs in Figure 7.11 demonstrates the modulus spectra ($M''$ versus $M'$) of all five compounds at different temperatures. The graphs show asymmetric and depressed arcs, which suggest
non-Debye dielectric relaxation and hopping type conduction, which is temperature dependent.\textsuperscript{126}

The variation of the real ($M'$) component of modulus as a function of angular frequency is also shown in Figures 7.11. $M'$ has a low magnitude at low frequencies and starts to increase gradually at higher frequencies. This increase can be attributed to the short-range mobility of charge carriers.\textsuperscript{126} As temperature increases, the onset of the rise in $M'$ shifts towards higher frequencies and the overall magnitude of $M'$ decreases, confirming the temperature-dependence of the relaxation processes.\textsuperscript{121, 126, 136}

As observed from the plots of $M'$ versus $\log\omega$, the frequency onset where the rise in $M'$ commences, is shifted to a higher frequency for the most conductive compound, $\text{Li}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{10}$ (shown in the last row of Figure 7.10), indicating better ionic mobility in this material. Figure 7.10 also shows the variation of the imaginary component of modulus ($M''$) as a function of frequency. The $M''$ spectra show peaks that shift to higher frequencies as temperature increases, indicative of the dependence of ionic mobility on temperature.\textsuperscript{121, 128} The peak position marks the frequency where a transition in the migration range of ions takes place.\textsuperscript{121, 126} At frequencies below the peak maximum, the mobility of charge carriers is long-range, and at frequencies above the peak maximum, they are short-range.\textsuperscript{121, 126} Furthermore, the non-Debye nature of relaxations, \textit{i.e.}, the occurrence of relaxation times with different time constants, is evident from the asymmetric shape of the peaks.\textsuperscript{49, 121, 126} It is noted that the positions of the $M''$ peaks for the most conductive compound, $\text{Li}_2\text{Ca}_2\text{Ta}_2\text{TiO}_{10}$, are shifted to significantly higher frequencies compared with the other materials. Therefore, the transition from long-range to short-range is pushed to higher frequencies, further showcasing the higher mobility of ions in this compound.
Figure 7.11: Complex modulus and its variation function with frequency. Each row shows the data for one of the five compounds, \( \text{Li}_2\text{A}_2\text{B}_2\text{TiO}_{10} \) (A= La, Sr, Ca; B = Ti, Ta).
7.8 CONCLUSIONS

The variation in the composition of the layered Li$_2$A$_2$B$_2$TiO$_{10}$ compounds, through the incorporation of different cations on the A and B-sites, results in the change in structure from a typical Ruddlesden-Popper structure to one featuring a supercell. The structural changes have a significant impact on enhancing the ionic transport properties in these materials. However, the hopping distances of lithium ions are also very important and appear to be a dominant parameter. The Sr$_2$-containing compound, which has long Li-Li distances, shows low ionic conductivity. Whereas the Ca$_2$-containing material with shorter Li-Li distances features enhanced conductivity, which can be confirmed by AC charge transport studies, impedance spectroscopy, and analysis of dielectric and modulus properties.
CHAPTER 8

CONCLUSION

The necessity for more efficient energy conversion and storage has powered the development of better and more affordable systems such as rechargeable lithium batteries. Commercial rechargeable lithium batteries are widely recognized for their use in most portable devices due to their high energy density and power performance. However, these batteries still have some safety challenges. Recent advances in battery technology have made the need for solid electrolytes, and consequently the all-solid-state lithium-ion batteries, more evident. Solid electrolytes can lead to improved safety, chemical and mechanical stability, a longer life cycle, and less expensive lithium-ion batteries. Some solid materials have been tested for this application. The features of materials with the Ruddlesden-Popper type structure make them promising candidates for this application. The ionic conductivity properties of the synthesized compounds were determined using the AC impedance technique. These studies reveal the potential of Ruddlesden-Popper oxides as Li-ion conductors.

Several strategies for the enhancement of lithium-ion conductivity in Ruddlesden-Popper oxide materials have been studied, through the synthesis of a series of $n = 2$ and 3 materials via solid-state approaches. The phase purity and structure of these compounds were characterized using powder X-ray and neutron diffraction techniques complemented with Rietveld refinement profile analysis. In enhancing lithium-ion conductivity in the $n =$
2 materials, two main strategies were explored. The first approach is through the shortening of Li-Li hopping distances, which was investigated through the substitution of larger cations such as Sr$^{2+}$ and Ta$^{5+}$ with smaller cations La$^{3+}$ and Ti$^{4+}$ at the A and B-sites, respectively. Unlike the larger cations, these substitutions with smaller-sized ions led to the formation of smaller unit cell volumes and ultimately shortened the hopping distances of lithium ions. Neutron diffraction analysis of samples that were made by this approach showed the shortening of Li-Li distance from ~2.80 Å in Li$_2$SrTa$_2$O$_7$ to ~2.75 Å, as captured in works from Chapters 2 and 4. The success of this approach was demonstrated from the enhanced conductivities measured for materials such as Li$_2$LaTaTiO$_7$ and Li$_2$LaNbTiO$_7$ at temperatures 100 °C and above. These pathways are also confirmed by DFT calculations, which showed the direction of lithium mobility pathways and further determined the energy barriers for each conduction pathway.

Secondly, we explored the impact of cation deficiency on the overall mobility of lithium ions, by inducing some amount of deficiency in the lithium layers. Creating defects in these layers led to the reduction in restrictions to ion mobility reported in materials of this structure type. Defects of this form, in general, have been known to affect the properties of solid materials in different ways. The ionic conductivity studies in the synthesized cation deficient materials Li$_{1.8}$LaTa$_{1.2}$Ti$_{0.8}$O$_7$ and Li$_{1.8}$LaNb$_{1.2}$Ti$_{0.8}$O$_7$, with 10% lithium deficiency showed conductivity values even at room temperature.

The effects of cation deficiency on the conductivity in the $n = 2$ members were further extended to $n = 3$ members. Here, cation deficiencies were induced in either inter- or intra-layer sites. Significant improvement was achieved via the cooperative effect of deficiencies at both inter- and intra-layer positions. The experimental results demonstrate
that the material with cation-deficiency on both sites (Li$_{1.9}$La$_{1.9}$Ti$_{2.6}$Nb$_{0.4}$O$_{10}$) showed extensively higher ionic conductivity than materials with deficiency on only one site. This observation is true even if the extent of cation-deficiency on both inter- and intra-layer sites is similar or lesser than those in compounds containing defects on only one of the two sites. To the best of knowledge, this is the first time such cooperative effects of material defects have been reported to impact the overall conductivity of materials of this structure. These observations indicate that the lithium-ion conductivity pathway can be within either the inter-stack or intra-stack spaces.

While defects seem to play significant active roles in enhancing the transport properties in these materials, symmetry transformations and supercell formation in these material types further enhance the observed conductivity in these oxide materials. Our investigations into the variation in the composition of layered Li$_2$A$_2$B$_2$TiO$_{10}$ compounds, through the incorporation of cations of different sizes on the A and B-sites, led to a change in structure from a typical Ruddlesden-Popper structure to one featuring a supercell (which is two times larger). These structural changes extensively impacted the ionic transport properties in these materials. The sizes of cations enhance or oppose the symmetry effects. Smaller-sized cations such as Ca$^{2+}$ were found to re-enforce the symmetry effect while larger cations such as Sr$^{2+}$ oppose the symmetry effect in these systems. Similar observations were made in a series of triple-layered materials which showed an improvement of conductivity values owing to the formation of supercells and the incorporation of smaller cations. The improvement in lithium-ion mobility achieved through these different strategies were confirmed by the dielectric and complex modulus
studies. These findings can be used for future research to design Ruddlesden-Popper oxides with enhanced lithium-ion conductivity.
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164


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**CURRICULUM VITAE**

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<table>
<thead>
<tr>
<th>Education</th>
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<tr>
<td>Doctor of Philosophy</td>
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<td>3.88</td>
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Peer Reviewed publications:

1. Fanah, S. J.; Yu, M.; Huq, A.; Ramezanipour, F., Insight into Lithium-Ion Mobility in \(\text{Li}_2\text{La(TaTi)O}_7\). *J. Mater. Chem. A* 2018, 6, 22152–22160

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7. Fanah, S. J.; Ramezanipour, F., Effect of Lithium Concentration and Distribution on Lithium-Ion Mobility in Layered Oxides Li$_2$La$_{1-x}$Li$_x$(Ta$_{2-y}$Ti$_y$)O$_7$ (x = 0, 0.25; y = 0.5, 1) (Under Review)

**Skills/Knowledge**

**Materials Design and Synthesis:** Accomplished the synthesis of several novel solid-state lithium containing materials through conventional solid-state methods for electrolyte applications

**Materials characterization methods:** Powder X-ray diffraction (PXRD), Scanning electron microscopy (SEM), Electrochemical impedance spectroscopy (EIS), thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), X-ray Photo-electron Spectroscopy (XPS), Nuclear magnetic resonance (NMR), Ultraviolet visible(UV/Vis), Infrared spectroscopy (IR)

**Software:** Ms Office, Origin, Diamond, Vesta, Zview, GSAS, ImageJ, Fullproof, Eis analyzer, Obs