Structural Modifications in the RbxCs$_{1-x}$PO$_4$ ($0 \leq x \leq 1$) Superprotonic Conductor Series: A Single-Crystal X-ray Diffraction and Impedance Spectroscopy Study

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STRUCTURAL MODIFICATIONS IN THE Rb_xCs_{1-x}PO_4 (0 ≤ x ≤ 1) SUPERPROTONIC CONDUCTOR SERIES: A SINGLE-CRYSTAL X-RAY DIFFRACTION AND IMPEDANCE SPECTROSCOPY STUDY.

ANDRES JOSE ENCERRADO MANRIQUEZ

Master’s Program in Physics

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Charles Ambler, Ph.D.
Dean of the Graduate School
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by

Andres Jose Encerrado Manriquez

2017
Dedication

This work is dedicated to my friends and family. To my spouse, Aileen, for being there with me throughout every step of the way, through sleepless nights as you caught the sleep that I couldn’t get. This work is also dedicated to my parents, Teresita Manriquez and Martin Encerrado, who first gave me the opportunity to pursue my dreams. Finally, to all of those friends who stayed with me throughout this path, who drank with me, laughed with me, and cried with me.

Thank you. It is over.
STRUCTURAL MODIFICATIONS IN THE Rb$_x$Cs$_{1-x}$PO$_4$ ($0 \leq x \leq 1$) SUPERPROTONIC CONDUCTOR SERIES: A SINGLE-CRYSTAL X-RAY DIFFRACTION AND IMPEDANCE SPECTROSCOPY STUDY.

By

ANDRES JOSE ENCERRADO MANRIQUEZ, B.S. in Physics

THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Physics
THE UNIVERSITY OF TEXAS AT EL PASO
May 2017
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Every single results described in this thesis was accomplished with the help and support of my fellow laboratory researchers and collaborators: Juan Leal, Ph.D., Alan Goos, Ph.D., and Victor Gonzalez. With their vast knowledge of chemistry and their scientific curiosity they patiently taught me and helped me understand the methods for synthetizing the different x values. Alan Goos and I worked together in a lot of research steps such as the Single Crystal analysis on the different x values; without his efforts this project would have taken a very different direction; I came to be greatly benefited from his sharp scientific insight and ability to translate complex ideas into simple terms. My fellow graduate researchers made this results possible due to the times that it took to prepare and analyze Impedance Spectroscopy samples, sometimes we will have to allocate specific times for each to come to the lab and prepare the samples during the weekends and nights, so here is a special acknowledgement to Israel Martinez, Andrea Montgomery, and Heber Martinez. Alex Price guided me through the understanding and the steps required to take with the Scanning Electron Microscope. He was extremely reliable during the whole process maintaining his occupations as advisor, lecturer and student all together.

Thank you to the laboratory Coordinator, Karla Carmona, for providing me with the opportunity to guide undergraduate students of different academic backgrounds and develop their interest in the field of Physics. Your efforts to reach out to people who would otherwise be uninterested in the field has shaped my own graduate experience.
The Department of Defense, thank you for your interest on the field of renewable energy and the financial support provided to complete this work.

Finally I would like to acknowledge my friends and family who supported me during my time here. I would especially like to thank my spouse Aileen Martinez for all the constant love and unyielding support throughout all the restless nights. Thank you also for helping me with your vast understanding and usage of the English language; this paper would have been a jumble of senseless words without your help.
Abstract

We have used single-crystal X-ray diffraction measurements to investigate the structural modifications induced by Rb-doping of the protonic conductor CsH$_2$PO$_4$. Data collected on the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ ($0 \leq x \leq 1$) series shows that the monoclinic P2$_1$/m CsH$_2$PO$_4$ presentation persists upon Rb-doping up until $x = 0.8$. Rb$_{0.8}$Cs$_{0.2}$H$_2$PO$_4$ exhibits a previously unreported P2$_1$/c monoclinic structure, where the mirror plane is lost and disorder is present in the PO$_4$ tetrahedra even at room temperature. Higher levels of $x$ display a tetragonal I-42d unit cell isomorphic with the known structure of RbH$_2$PO$_4$. The temperature dependence of the proton conductivity determined from impedance spectroscopy data collected within the 160$^\circ$C-250$^\circ$C range is also markedly different at high Rb-doping levels, $x = 0.8$. Finally, Rb$_{0.9}$Cs$_{0.1}$H$_2$PO$_4$ undergoes a transition from its room-temperature tetragonal I-42d phase to an intermediate-temperature monoclinic P2$_1$/m modification at a significantly lower temperature (~80 $^\circ$C) than pure RbH$_2$PO$_4$ (~120 $^\circ$C).
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<th>Description</th>
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<tr>
<td>ACEIS/EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>CDP</td>
<td>Cesium Dihydrogen Phosphate, CsH2PO4</td>
</tr>
<tr>
<td>RDP</td>
<td>Cesium Dihydrogen Phosphate, RbH2PO4</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>SCXRD</td>
<td>Single Crystal X-ray Diffraction</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline Fuel Cell</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer Electrolyte Membrane Fuel Cell</td>
</tr>
<tr>
<td>DMFC</td>
<td>Molten Carbonate Fuel Cell</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>SAFC</td>
<td>Solid Acid Fuel Cell</td>
</tr>
<tr>
<td>RFC</td>
<td>Reversible Fuel Cell</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

Fossil fuels continue to be the main source of energy for most industrialized nations despite the desire for alternative energy. According to the National Academy of Sciences, nearly 30% of all fossil fuel used is consumed by the transportation sector which includes personal vehicles, large trucks, and freight trains. Emerging technology that could replace fossil fuel burning engines with green alternatives would greatly reduce our carbon footprint, thus reducing the current demand for oil.

Hydrogen fuel cells have been the focus of many research groups in recent decades with the goal of making an efficient, greenhouse emissions-free energy source. The combination of hydrogen and oxygen to produces electricity and water with no CO₂ exhaust. While other areas of research on this topic include hydrogen storage and catalysis, our attention is focused on the electrolyte that enables proton mobility. In this Chapter, we will outline the basic ideas necessary for the background of the project including key terms and concepts.

1.1 – Fuel Cells

Fuel cells are devices that convert the chemical energy from a fuel, in this case hydrogen, into electrical energy via an electric current. Conventional batteries are recharged and discharged by changing the supplying current or resistance whereas with a fuel cell is a constant flux of fuel that sustains a reaction and produces usable current. Fuel cells have recently become a popular topic of research due to the need for emissions-free transportation. Research to date has produced and tested prototype and concept vehicles.¹ ²

1.1.1 – Fuel Cell Origins

The concept of a fuel cell as a means to convert energy through electrochemical reactions has been around since the middle of the 19th century. The principle behind it was first discussed by a university professor at the University of Basle, C. Friedrich Schöbein, who is famous for
discovering ozone. The invention, however, is attributed to William R. Grove, who was in contact with him at the time and developed the first gas voltaic battery. Some of his other contributions include the first correlation of physical forces or better known as the conservation of energy.

1.1.2 – Fuel Cell Components and Processes

Fuel cells are composed of an anode, a cathode, and an electrolyte. The electrolytes’ role is to allow positively charged hydrogen ions (protons) to move between the two sides of the fuel cell. Figure 1 shows the basic structure of a common hydrogen fuel cell.

The platinum electrode at the anode end acts as a catalyst that oxidizes the hydrogen fuel generating protons and electrons. These positively charged ions are attracted towards the cathode and migrate through the electrolyte. The electrons flow through an external circuit towards the cathode and produce a current. At the cathode, the protons, and reduced oxygen react to form the only byproduct: water.

Figure 1: Diagram of a hydrogen fuel cell
1.1.3 – Fuel Cell Classifications and Their Applications

Fuel cells are classified by the type of electrolyte they use and by the difference in startup time. From those two factors, efficiency, durability, and their properties can be easily understood.

The first type is classified for low temperature operations because it can’t persist above 200 ºC it’s called Alkaline Fuel Cell (AFC) also known as the Bacon Fuel Cell because of its British inventor, Francis Thomas Bacon. This is one of the most fabricated fuel cells due to its accessible technology; NASA has used them in the Apollo-series missions and on the Space Shuttle. They consume hydrogen and pure oxygen to produce potable water, heat, and electricity. They are among the most efficient fuel cells producing 5kW-150kW net output and reaching an efficiency of 70%.

The Polymer Electrolyte Membrane (PEMFC) is noted for its fast startup time: 1 second for proton exchange; it has been developed for transport applications as well as stationary fuel cell. Depending on the electrolyte, they can withstand low operating temperature between 40ºC – 100ºC and they are the prime candidates to replace its predecessor the Alkaline Fuel Cell technology.

Direct Methanol Fuel Cells (DMFC), the DMFCs are powered by pure methanol which is in most cases mixed with water when it reached the anode, whereas most fuel cells use hydrogen as its fuel and its feed directly or inside the same fuel cell by reforming hydrogen-rich fuels such as methanol or ethanol. One of the advantages with this type of fuel cell is that methanol is easier to store and transport than hydrogen; additionally, with the current system in place for gasoline disposal it would be easier to adapt so that it becomes accessible to the public.

They are also under the category of proton-exchange fuel cells, but they have a much lower efficiency so they are mostly used for portable technology where efficiency is less important and there are smaller power output demands, e.g. ~5kW. One noted disadvantage is carbon dioxide production along with water emissions. The operation temperatures are between 60ºC –130ºC which pose a great limitation for fuel safe storage.

Phosphoric Acid Fuel Cells (PAFC), currently the benchmark with one of the highest efficiency ratings measured at 80% – 85% when generating electricity and heat together; when
generating electricity alone efficiency is 37% – 42%. Outputs have also been successfully increased with cells producing anywhere from 50kW-11MW net power. Operating temperatures are intermediate, between 160ºC– 220ºC.

They are tolerant of impurities in fossil fuels that have been reformed into hydrogen unlike PEMFCs which are easily contaminated by carbon monoxide. On the downside, PAFCs are known to be larger and heavier, making them less efficient in transportation applications.

**Solid Acid Fuel Cells (SAFC)** are a class of fuel cells that are characterize by the use of a solid acid compound as their electrolyte, it works very similar to the proton exchange membrane fuel cell and to that of solid oxides. They obtain electricity from an electrochemical reaction of converting hydrogen ions and oxygen gases and leaving only behind a byproduct of water. Their operation temperatures are between 200 ºC and 300 ºC.

Current systems of Cesium Dihydrogen Phosphate (CDP) have demonstrated lifetimes of thousands of hours under certain conditions sustained after the superprotonic phase transition. In 2014 a toilet that chemically transform waste into water and fertilizer was develop using a combination of solar power and SAFC.

**Molten Carbonate Fuel Cells (MCFC),** use a molten carbonate salt, *e.g.* lithium carbonate, suspended in a porous ceramic matrix as an electrolyte. The operation of this membrane occurs at high temperatures within the range of 600ºC -800ºC. They reach efficiencies approaching 65%, and have been coupled with turbines in order to increase overall efficacy.

At the high temperatures at which it operates, methane and other light hydrocarbons are converted to hydrogen within the fuel cell, called internal reforming, allowing a range of fuels to be used. They are less cost effective than most fuel cells, but the primary disadvantage is the durability, because of the same high temperatures of operation accelerates breakdown and corrosion.

**Solid Oxide Fuel Cells (SOFC)** operate at very high temperatures ranging from 600ºC – 1000 ºC which makes it the highest operating temperatures of all fuel cells. The electrolyte is a solid ceramic, *e.g.* zirconium oxide stabilized with yttrium oxide. As with the MCFC the high
operation temperatures makes it possible to reform the fuels inside the fuel cell itself. They are tolerant of carbon monoxide which can be used as fuel, allowing natural gas and gases made from coal to be used.

One of the disadvantages is that the high operating temperatures put a lot of strain on the materials so the durability is lower, and it can take longer to start up due to the high temperatures it has to reach. They produce between 100 – 250kW net power.

**Reversible Fuel Cells (RFC),** the technology of reversible fuel cells is currently in development. As other fuel cells it produces electricity and oxygen and generates heat and water as byproducts. The main difference is that these can use electricity from solar power, and other sources to split water into oxygen and hydrogen through electrolysis which proves to be a great advantage over others. The Table 1 below presents a summary of the different fuel cell types, the differentiation between them, characteristics such as what are the ranges of temperature at which they operate, the type of fuels the cell can tolerate, and the composition of the electrolyte. Aside from temperature, other operation conditions such as humidity, pressure, and gasses present, among others have the ability to affect the conductivity on these electrolytes (Noted in literature when the CDP, a solid acid electrolyte, is kept under constant pressure of 1GPa in a diamond anvil cell its stability in its most conductive form is preserved) \(^3, 4, 5\)
Table 1: Types of Fuel Cells and Characteristics

<table>
<thead>
<tr>
<th>FC</th>
<th>Transport Mech.</th>
<th>Op. Temperatures(°C)</th>
<th>Type of Electrolyte</th>
<th>Type of Fuel</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>Grotthuss</td>
<td>40-200</td>
<td>KOH</td>
<td>H₂</td>
<td>NASA</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Grotthuss</td>
<td>40-100</td>
<td>Polymer</td>
<td>H₂/CO₂</td>
<td>Transport/ Industrial</td>
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<tr>
<td>DMFC</td>
<td>Mixed</td>
<td>60-130</td>
<td>Polymer</td>
<td>Methanol</td>
<td>Electronics</td>
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<tr>
<td>PAFC</td>
<td>Grotthuss</td>
<td>160-220</td>
<td>Phosphoric Acids</td>
<td>H₂/CO₂</td>
<td>Industrial/Commercial</td>
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<tr>
<td>SAFC</td>
<td>Grotthuss</td>
<td>200-300</td>
<td>Solid Acids</td>
<td>H₂/others</td>
<td></td>
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<tr>
<td>MCFC</td>
<td>Grotthuss/Mixed</td>
<td>600-800</td>
<td>Molten Carbonate</td>
<td>CH₄, H₂, CO</td>
<td>Military / Industrial</td>
</tr>
<tr>
<td>SOFC</td>
<td>Grotthuss</td>
<td>600-1000</td>
<td>Solid Oxide</td>
<td>CH₄, H₂, CO</td>
<td>Power Generators</td>
</tr>
</tbody>
</table>

One of the first applications of hydrogen fuel cells beyond proof-of-concept came in the NASA space program, with implementation in spacecraft from satellites to manned space capsules. Since then, fuel cells have become of great interest and many new applications have been sought after. Fuel cells are used for power in commercial, industrial, and residential buildings as well as in remote or inaccessible areas.

They also became popular in the race for the “zero-emission vehicle” to replace the currently fossil fuel based personal transportation solutions of automobiles, buses, boats, and motorcycles. Another recent implementation include the powering of different modern tools, from cellphones to planes, such findings have been the focus of Large green-energy focused symposia like the Electric and Hybrid Vehicle Technology expo and the Renewable Energy World International, during which scientists and industry officials present their newest findings and technology and fuel cells are shown to power many different modern tools from cellphones to trucks.
The focus of our study is the proton transfer media within the heart of the fuel cell. Solid acid electrolytes are the base of great study because of its ease of production and the physical properties they exhibit, maintaining the properties of salts and acids the electrolytes can be easily dissolved in water to form an electrically conducting solution, and it can be recrystallized by the means of supersaturation and filtration.

The most commonly known material to be used as electrolyte is Nafion, which is a sulfonated tetrafluoroethylene based on a fluoropolymer form discovered by scientists at the DuPont Corporation. It has the attention of the fuel cell community because of its relative thermal and mechanical stability, but its conductive properties remain the focus of research all over the world; this has already many applications in the modern societies for fuel cell applications and sensors. Nafion was introduced 40 years ago and has become the industry’s number one fuel cell electrolyte material for applications at low temperatures Nafion, requires a humidified atmosphere which limits its operational temperature range.

However, focus has shifted away from the effective temperature range of Nafion which starts to lose its conductive properties above 80 °C. Research on the topic of phosphate solid acids, such as CsH2PO4 (CDP) and RbH2PO4 (RDP) shows promising properties at intermediate
temperatures,\textsuperscript{3} CDP, in particular, has proven a sharp proton conductivity increase, up to $10^{-3}$–$10^{-2}$ S·cm$^{-1}$, upon heating to ~235°C.\textsuperscript{2–5}

The focus of our research includes the synthesis and characterization of a series of solid acid electrolytes for the system of Rubidium-Cesium Dihydrogen Phosphate from ratios of a given value of $x$ ($0 \leq x \leq 1$) for this purpose we used Energy Dispersive Spectroscopy. The analysis technique that hasn’t been used before in terms of structural characterization, was Single Crystal X-ray Diffraction which allow a deeper understanding of these compounds. Of course we are concerned about the relation between the crystal structure in relation with the doping ratio $x$ and the conductivity exhibit at these ratios over a range of temperatures, for which purpose we used Alternating Current Electrochemical Impedance Spectroscopy in a sophisticated sample holder that can recreate the conditions of a fuel cell.\textsuperscript{6, 7}

1.2 – Solid Acid Compounds

Solid acids are composed of salts of strong polyprotic acids, and have been shown to have mobile protons in their structures under certain conditions. Some well-known solid acids consist of aggregate added structural material such as carbon, zirconia, and silica. They share the physical properties of many ionic salts; for example the transparent coloration as a single crystal and white appearance as an aggregate, their high solubility in water, however what differentiates them from many ionic salt is their decomposition at high temperatures. Additionally exhibit high solubility in water; when in solution they undergo a process of hydrolysis they undergo when in a solution that produces hydronium ions in water.

Acid salts are compounds that possess properties of both salts and acids, due to an incomplete replacement of the hydrogen of a polyprotic acid. They have gained new attention from the fuel cell community since they are able to operate at intermediate temperatures and show promising properties regarding their protonic conductivity.\textsuperscript{8}
In a fuel cell the electrolyte is at the center of the system where it carries the charged particles, in this case hydrogen ions, from one electrode to another. The electrolyte must be permeable to the ions while separating anode and cathode, in fact, the type of electrolyte used is the primary classification of the cell. These decisions include the size of the fuel cell, the fuel that is going to be used, and the type of electrodes.

An electrochemical reaction is a process caused or accompanied by the production of an electric current. In a fuel cell the reaction is used to generate an electric current in electrochemical cells, gaseous oxygen and hydrogen can be combined to form water and usable current.

1.2.1 – Superprotonic Behavior

Solid acid compounds possess properties of both acids and salts and some are known to undergo a “superprotonic” phase transition where the conductivity jumps in several orders of magnitude. This phenomena has been well studied with several compounds of the category of $\text{MHXO}_4$, $\text{MH}_2\text{XO}_4$, $\text{M}_1-x\text{MxH (XO}_4)_2$, and $\text{M}_3\text{H (XO}_4)_2$, where $M = \text{Cs, NH}_4, \text{Rb, K}$ and $X = \text{S, P, Se}$. Because they share properties of salts they are water soluble; they also share similarities on the structural behavior: they undergo a transition to superprotonic phase first at intermediate temperature, then gaining stability under that range of temperatures to finally dehydrate under high operating temperatures for fuel cells on the 260ºC.

1.2.2 –Grotthuss Mechanism

The process by which protons migrate within a solid is often referred to as “Grotthuss mechanism” (or Bucket Brigade Mechanism) which allows the diffusion of available protons through a hydrogen bond network; this process is correlated with increases of temperature because of the higher magnitude of vibration of the protons, facilitating the transfer process to a nearby binding site (Figure 3).
1.2.3 – Prior Applications

The prior studies presented by the Cristian Botez research group on Cesium Dihydrogen Phosphate (CDP) presents a well described experimental procedure from the temperature range 20 - 300ºC that details of the monoclinic samples at room temperature as well as the phase transition to the cubic phase and correlates with the increase on the conductivity, also known as a superprotonic conduction phase. They have also documented the high temperature of loss of stability and dehydration of the sample over time.¹²

Other results from the Botez group on Rubidium Dihydrogen Phosphate (RDP) detail the tetragonal samples undergoing a phase transition into a monoclinic structure, a phase shared by CDP.¹³

The reported temperatures under ambient pressure go as follows: monoclinic to cubic phase structural transition at T = 237ºC; slow dehydration starts prior to these temperatures and continues even in the absence of further heating; the dehydration is no complete with significant amount of cubic CDP remaining in the sample 2 hours after the transition.

Most phosphate salts undergo similar behavior: a phase transition (not necessarily cubic) at very close temperatures, followed by the slow dehydration over time, and finally, when temperature increases, a complete loss of morphology. Other studies have been conducted on Rubidium Dihydrogen Phosphate (RDP), Rubidium Deuterium Phosphate (DRDP), which follow this pattern.¹²
Chapter 2: Aim of Study

Research into materials that can act as effective proton conductors at intermediate and high temperature is important to the future to the wide spread adoption of hydrogen fuel cell technologies.

Our project includes the synthesis and characterization of a series of solid acid electrolytes for a system of cation substitution of Rubidium in Cesium Dihydrogen Phosphate from ratios of a given value of $x$ ($0 \leq x \leq 1$). Energy Dispersive Spectroscopy was used in conjunction with results obtained with SCXRD to assure that the synthesis results were correct before moving forward.

Single Crystal X-ray Diffraction is a very well-known tool for crystallographic characterization that allows a deeper understanding of the materials. It will allow us to better understand the relation between the crystal structure and the metal doping ratio “x”.

AC conductivity measurements took place to better appreciate the dependence of this factor “x” over the ratios at range of temperatures, for which purpose we used Alternating Current Electrochemical Impedance Spectroscopy in a sophisticated sample holder capable of simulating the conditions existing inside a fuel cell, including the flow of two different gasses on opposite sides of the pellets.\(^7\)

2.1 – Prior Study

It has been shown that superprotonic phases of solid acids display a high symmetry (i.e. cubic or tetrahedral) in their crystalline forms with energetically available sites for hydrogen bonding more numerous than the protons present. For phosphate-based solid acids, the mobility of the protons at elevated temperature may be linked to disordered positions for the PO\(_4\) groups, since H\(_2\)PO\(_4\) groups rotate and nearby hydrogen bonding sites become close enough to make the transfer of a proton.\(^{12,16}\) On several studies focused on CDP,\(^{18-20}\) it was suggested that partial replacement of the cation Cs\(^+\) by Li\(^+\), K\(^+\), or Rb\(^+\) may tune the properties of the material and improve the measured proton mobility.
Likewise the HSO$_4^-$ anion was introduced for the same ends. Structural changes due to ion replacement were suggested as the cause of the changes in conductivity because structure affects the barriers to rotational disorder and therefore proton mobility. However this is not the only explanation for higher conductivity within these materials, there has been a robust debate on the origin of the high temperature enhanced proton conductivity of CDP. Park et al. and Ortiz et al. have supported that this phenomenon is due to thermal decomposition and partial transformation to a pyrophosphate. Others, like Brownowska, Baranov et al., Boysen et al. and Botez et al. argue that the increased proton conductivity is due to a polymorphic phase transition to a cubic structure.

Reinforcing any of these hypotheses requires corroborating proton conduction measurements with structural investigations that, in the case of phosphate solid acids, have been so far exclusively carried out using powder X-ray diffraction.

2.1.1 – Materials of Interest

Previous research found that Solid Acid materials, materials based on Alkali metals and phosphate or sulfate which include Cesium Dihydrogen Phosphate (CDP) and Rubidium Dihydrogen Phosphate (RDP), show promising results for proton transport. Doping or combinations of CDP and RDP, like the solid-state structures of Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ (0 ≤ $x$ ≤ 1), is the subject of this research, beginning with the goal of identifying Rb-doping induced atomic-level structural modifications using Single Crystal X-ray Diffraction.

The jump in the proton conductivity of CDP at ~235°C is attributed to a phase transition from CDP’s room-temperature monoclinic phase to a cubic phase (the superprotonic phase), as indicated above. We are interested in how the cation ratio affects the temperature at which phase changes take place and how this affects proton conductivity.

While the room temperature crystal structure of RDP is tetragonal, we have recently reported an intermediate-temperature transformation to an RDP phase that is monoclinic and isostructural to room-temperature CDP. ADD SOSSINA PAPER ON CDP PRESSURE
2.1.2 – Analysis Techniques

Previous powder x-ray diffraction results have shown a dependence of the lattice parameters on the proposed system of Rubidium and Cesium ratio. Using SCXRD data we will allow for a more precise determination of atomic structures and atom positions; this in turn will reveal the changes of symmetry that it undergoes providing a greater insight into the structural pathways for proton conduction. In this work we also aim to investigate phase changes, similar to the tetragonal-to-monoclinic phase change reported in RDP, within the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ series.

Temperature resolved impedance spectroscopy carried out on Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ samples of different x values, in conjunction with high-quality structural data, will help clarify the effect of the Rb-doping-induced microscopic structural changes and their effect on the macroscopic proton conductivity properties of these materials.
Chapter 3: Methods and Materials

This Chapter will address the background necessary to understand the project’s execution, and the specific techniques used for analysis and the basics of some of these techniques as well as the physics behind them. The first section is dedicated to the process of synthesis of materials with the ratio of metals desired. Then we will talk about Single Crystal X-ray Diffraction and the analysis of the data as well as the methods used to corroborate material characterization as well as structural determination. Finally we briefly demonstrate the foundation for AC Electrochemical Impedance Spectroscopy and the methods we used for the analysis of the data.

3.1 – Synthesis Process

In this section we describe the process used in the production of mixed-metal materials along with the table of the proportions used to get the appropriate ratios of Rubidium and Cesium Dihydrogen Phosphates.\textsuperscript{32, 33}

Samples of $\text{Rb}_x\text{Cs}_{1-x}\text{H}_2\text{PO}_4$ ($0 \leq x \leq 1$) were synthesized from a mixture of phosphoric acid and desired ratio of $\text{Cs}_2\text{CO}_3$ and $\text{Rb}_2\text{CO}_3$ in distilled/deionized water. Slow evaporation was used to grow high quality crystals, this was necessary when growing crystals suitable for SCXRD. This process was used to create Rb doped samples of desired concentrations.\textsuperscript{34}

$$x \text{Rb}_2\text{CO}_3 + 1 - x \text{Cs}_2\text{CO}_3 + 2 \text{H}_2\text{PO}_3 \rightarrow 2\text{Rb}_x\text{Cs}_{1-x}\text{H}_2\text{PO}_4 + \text{H}_2\text{O} + \text{CO}_2$$

Equation 1: Stoichiometry followed for the synthesis of the conductor series

In Equation 1 we have the general reaction scheme followed to calculate the ratios of carbonate required. Underneath in Table 2 we have the ratios used for the production of materials in grams.
### Table 2: Stoichiometry calculations for the synthesis process of slow evaporation

<table>
<thead>
<tr>
<th>Cs</th>
<th>Cs₂CO₃ (g)</th>
<th>Rb₂CO₃ (g)</th>
<th>H₃PO₄ (g)</th>
<th>Final product (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>.6520</td>
<td>4.160</td>
<td>4.611</td>
<td>9.423</td>
</tr>
<tr>
<td>20%</td>
<td>1.303</td>
<td>3.695</td>
<td>4.611</td>
<td>9.609</td>
</tr>
<tr>
<td>30%</td>
<td>1.954</td>
<td>3.233</td>
<td>4.611</td>
<td>9.798</td>
</tr>
<tr>
<td>40%</td>
<td>2.606</td>
<td>2.771</td>
<td>4.611</td>
<td>9.928</td>
</tr>
<tr>
<td>50%</td>
<td>3.258</td>
<td>2.309</td>
<td>4.611</td>
<td>10.178</td>
</tr>
<tr>
<td>60%</td>
<td>3.909</td>
<td>1.847</td>
<td>4.611</td>
<td>10.367</td>
</tr>
<tr>
<td>70%</td>
<td>4.561</td>
<td>1.384</td>
<td>4.611</td>
<td>10.556</td>
</tr>
<tr>
<td>80%</td>
<td>5.212</td>
<td>0.922</td>
<td>4.611</td>
<td>10.655</td>
</tr>
<tr>
<td>90%</td>
<td>5.864</td>
<td>0.459</td>
<td>4.611</td>
<td>10.934</td>
</tr>
</tbody>
</table>

3.2 – Single-Crystal X-Ray Diffraction (SCXRD)

Single-Crystal X-Ray Diffraction (SCXRD) is a characterization technique used to find precise atom positions within a material and therefore its microscopic structure. The relationship of the structure of solid acids electrolytes on their bulk physical properties, i.e. proton conduction, is not well understood. In this section we will talk about the basics of the technique along with the process of sample selection and the analysis of the data obtained.

3.2.1 – SCXRD Basics

Single-Crystal X-Ray Diffraction (SCXRD) is a technique for the analysis of crystalline substances. It is capable of providing very detailed information about the internal lattice of the samples: unit cell dimensions, bond lengths, and bond angles. The development of this technology was in parallel with the Powder XRD, and also uses an X-ray tube to produce collimated radiation that is directed to the sample, while the detector stands behind the target. All methods are based
on the generation of X-rays in an X-ray tube and the detection of reflected X-rays. The main differences in the techniques are in the sample choice and in the detector area.

Data produced from samples consists of several thousands of unique reflections whose arrangement is called a diffraction pattern. The Miller Indices (hkl) may be assigned to each reflection to indicate its position within the pattern, this has a Fourier relationship to the crystalline lattice and the unit cell in real space.

3.2.2 – SCXRD Methods

In the Figure 4 image we can see 3-circle diffractometer with the angles between the incident ray, the detector and the sample marked.

![Figure 4: Single Crystal Optics Schematic with a 3-circle goniometer head](image)

Single Crystal X-ray Diffraction experiments took place in the Scattering Laboratory under the supervision of Dr. Cristian Botez in a brand new Bruker D8 Quest with 3-circle goniometer equipped with a Photon 100 CMOS detector. When non-ambient environment was required, we had Oxford Cryostream system was equipped to allow for the control of the temperature of the
samples in an orderly way warming up a nitrogen stream from 100 K to 400 K. The light source comes from a Molybdenum (Mo) monochromatic radiation Kα (λ = 0.71073 Å) that was focused via Triumph multilayer optics.

The selection of a single crystal sample involved a Polarized Light Microscope and a micro-tools. The crystal is placed in a highly viscous oil (Paratone-N, Hampton Research) to make its manipulation, transport, and adhesion to the sample stage (micro loop by MiTeGen) possible.

The crystal cluster is placed under the microscope’s polarize light in order to detect fractures and cracks on the crystals as well as entanglement with others because we have to make sure the sample is, in fact, a single crystal. The size of the crystal must be well suited to both the sample stage and the size of the X-ray beam.35

After the sample was mounted into the goniometer and it was adjusted to align with the beam and the data was collected, gathering hundreds of images for analysis. Data were reduced and processed using the Bruker Apex II suite of programs. A multi-scan absorption correction was calculated and administered using SADABS 36 and the structures were solved by SHELXT sub-routines included in APEX II.36, 37 Atoms were located using a Fourier difference mapping technique, and structures were eventually refined by full matrix least squares algorithms on F.36, 39 Hydrogen atoms were placed geometrically using a riding model. All non-hydrogen atoms were refined anisotropically.
3.2.3 – SCXRD Data Output

Some of the data is shown in Figure 5 were each one of the spots is a reflection, a contribution from the planes of atoms in the crystal. It is necessary to collect as close to 100% of the unique reflections up to a desired resolution to create a real-space image; the information about the position and the intensity of the diffraction pattern is collated and analyzed. The reflections contain information to construct a structure of the material at the atomic level. Single Crystal X-ray Diffraction was carried out on a Bruker D8 Quest with a 3-circle goniometer equipped with a Photon 100 CMOS detector.

We collect hundreds of images like these during the measurement and they are reduced and analyzed with Bruker Apex II software. Now each one of the images contains reflections that

Figure 5: Single Crystal X-Ray Diffraction Pattern, raw data obtained from RDP at transition temperature
make up the total diffraction pattern which undergoes a Fourier transformation that will allow us to produce an electron density map which is the basis of atomic model of our materials.\textsuperscript{35,40-42}

3.3 – Energy Dispersive X-Ray Spectroscopy (EDS)

EDS has been used to characterize the chemical composition of samples. During this section we will discuss the origin of this technique as well as its application in our experiments. This was the first set of experiments we performed because it was important to make sure that the synthesis resulted in the desired ratios of metals.\textsuperscript{43}

3.3.1 – EDS Origins

Energy Dispersive X-ray Spectroscopy or EDS was developed in the 1950s by Ernst Ruska and Max Knoll. It belongs to the family of Electron Microscopes (Transmission Electron Microscopes or TEM and Electron Backscatter Diffraction or EBSD); Figure 6 presents a simplified view of the process. The sample is placed at the base and the chamber is evacuated to obtain a vacuum.\textsuperscript{43, 44}

![Figure 6: Schematics of a Scanning Electron Microscope and Energy Dispersive Detector](image)
The microscope produces images by shooting a focused beam of electrons that interact with the atoms in the sample which generate signals with information about the topography and chemical composition of it. It works by scanning the surface of samples by measuring the emitted secondary electrons from it. It creates images with magnification greater than that of optical microscopes. This makes it the perfect tool for many fields including biology, forensic science, physics, etc.

The electron beam hits the sample and excites it so it emits X-rays of a characteristic wavelength; the sample becomes ionized by the incident beam and start to eject electrons from the lowest energy levels. This action happens to release energy and this is the characteristic emission from each element when it happens to have many elements present of a wavelength dispersive spectrometer.43-45

![Tabletop Microscope TM-1000](image)

**Figure 7**: HITACHI TM-1000 Energy Dispersive X-Ray Analyzer

### 3.3.2 – EDS Methods

Energy-Dispersive X-ray Spectroscopy (EDS) data were used to confirm the expected Cs: Rb ratio for all the samples used in this study. The measurements were performed on an Oxford Instruments attachment integrated into a Hitachi TM-1000 (Figure 7) system and the data was analyzed using SwiftED software.46
3.3.3 – EDS Output

The EDS technique relies on a pulse height analysis. The detector gives a reading proportional to the height to the X-ray photon energy, it is used in conjunction with a pulse height analyzer. The detector will determine the resolution of these refracted beams and a program will determine the weight presence of the element in percentage contained in the sample.

The data is presented in a graph with the X-axis representing the X-ray energy (in eV wide usually) and the Y-axis being the number of counts per channel. An energy line that is consistent with the individual energy of the photons is then broadened by the system to produce a Gaussian profile and the energy resolution is then defined by the full width of the peak at half maximum height (FWHM). The analysis is done by the identification of the line and doing a quantitative analysis which comes very handy to obtain a complete spectrum. 47

3.4 – AC Electrochemical Impedance Spectroscopy

AC Electrochemical Impedance Spectroscopy is a technique required to obtain the ionic conductivity of solid acid electrolytes. This segment will address the basic theory behind this technique as well as the experimental process we followed.

3.4.1 – Impedance Spectroscopy Origins

This method was devised by applying several analysis techniques to the basic understanding of Ohm’s Law of current and voltage, where the current and voltage signals from an AC source are analyze and their phases compared with each other, this phase shift then is used together with Ohm’s Law to calculate the Impedance of the system, we shall discuss latter on the possible representations of the data. 48
3.4.2 – Impedance Spectroscopy Data and Analysis

For solid acid compounds this is a very commonly used technique, because if you were to apply a DC current to the solid electrolytes it only produces a polarization that then stops the ions from moving in one side of the electrodes basically creating a electrolyte capacitor.

In Impedance Spectroscopy with an AC voltage the ions oscillate in parallel to the direction of the current which is directly proportional to the frequency voltage.

\[ Z = \frac{E_0}{I_0} \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \]

**Equation 2**: Impedance calculation analogous to Ohm’s Law

The accurate and absolute value of the impedance \( Z \) can be obtained by the voltage, current and phase shift from a Cole – Cole plot. The most commonly graph used to measure the conductivity is the Nyquist Plot which uses the bulk resistance of the material, the surface area of the electrodes and the separation between them represented in this plot. Through a derivation of the Nernst-Einstein relation we can calculate the ionic conductivity of the samples.

\[ B(2\theta) = \frac{K\lambda}{L\cos(\theta)} \]

**Equation 3**: Nernst-Einstein Relation

In Figure 1.8 we can see an example of an equivalent circuit (Randles cell) can be seen, which is the basic set up used to compare to the measured results of EIS results, the models can become very complicated and it depends on the quality of the data obtained. The software used to analyze it is called ZMAN, it works as a recognition software for the industry where it takes a preexisting circuit model and changes the values for the components to better match the results from each sample; it does this process for hundreds of possible circuit combinations and provides the best matches to be then used for the calculations of the conductivity.
In order to better understand the behavior of the transport mechanics and the relevance to the real conductivity of the materials, these representations are calculated by a software which gives certain values to them to better fit the experimental and theoretical data. Here the $R_s$ is the uncompensated solution resistance, $R_p$ is the polarization resistance, and $C_{dl}$ is the double layer capacitance. \textsuperscript{49, 50}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{randle-cell.png}
\caption{Simple equivalent circuit (Randles cell)}
\end{figure}
3.4.3 – Impedance Spectroscopy Preparation and Assembly

The sample holder that makes this type of measurement possible is called ProboStat and is fabricated and distributed by NorECs. It’s a chamber is designed quote - “for measurements of electrical properties, transport parameters, and the kinetics of materials, solid/gas interfaces and electrodes under controlled atmospheres at high temperatures up to 1600°C.”

It possesses a wide range of accessories for the system developed by the experiences of Kofstad/Norby group at the University of Oslo. The sample in question rests on a long support tube of alumina inside a closed outer tube of alumina/silica. The sample can be connected with 2 to 4 electrodes of platinum, using a disk, a van der Pauw, or bar geometries. Everything is held together on top by a spring loaded alumina section to hold the sample and electrodes together and in place. ⁷

It has 16 electrical feedthroughs allowing the use of many measurement apparatus simultaneously. Gasses can be fed in single or dual chamber modes directly onto or from

---

Figure 9: Sample Holder for the Impedance Spectroscopy, the ProboStat
electrodes, allowing for many combinations and incredible control of the atmospheres surrounding
the samples.

The assembly of the ProboStat start by selecting what set up we are going to be using, which includes how many temperature controls we need, if we are going to flow any gases trough the sides of the pellet or not, if we need a transparent enclosing or an obscure one, then we assembly the ring stand by removing it from its box and securing it to the assembly node.

Take away the protective encasing and start with the first chamber which is the one controlling the gas flow underneath the sample, we need to make sure that the electrodes are properly connected because they are essential to the calculations of connectivity latter on.

Following goes in the enclosing of the first electrode or anode (at which point we can bend the wire mesh on top of the opening) along with the first gas intake of the system. Immediately afterwards assemble the spring compression system which are three ceramic rods that slide into a holder that allows flow of gas from the top (to flow gases just like in a fuel cell), we put it aside for the moment.

For the cathode assembly we need to connected on the outside of the first enclosing and we can then start to set up the material by placing the pellet on top of the lower mesh and then alighting the second mesh on top of it, now we can set up the previously assembled spring compression system, which consists of 3 springs to hold them together (different tensions are possible so depending on the sample we can vary it).

After the top mesh is bend inside, carefully lower the compression system and attach the three spring by stretching them to the lower section of the base. Then we can attach the cathode gas tube and the thermocouples to the base and hold it right on the top entrance of the compression system where the hole is located, during this same step the thermocouples are connected.

Finally we grab the outer enclosing and slide over every piece of the ProboStat so it fits tightly together, outside we secure it with a screwing base on it.

After its place on a secure location underneath the tube furnace we can attach the proper confections, first the temperature sensors are connected, depending on the experiment we can use
several at one time, for example on humid environment experiments the temperature control that will tell us the temperature of the base is added, this base has to be above water boiling point to avoid deposits on the base. Never forget to connect the thermocouple sitting millimeters away from the sample so we obtain accurate readings.

Then we connect the coaxial cables from the Impedance / Phase Gain Analyzer Solartron then, again if we are doing experiments that required a humid environment we connect the humidity control box and heating system so we make sure that we are bubbling the water on to the system and not just deliver water on the sample which could pose obvious problems.

After that we set up the sweeping program for the desired range of analysis as well as the collecting software so we can see the data captured in real time as a Nyquist plot.

As previously explained for the accurate calculations of the impedance of the material there needs to be strict control over the physical characteristics of the pellets due to the direct effect on their surface and the distance in between electrodes.

Different set ups for the experiments will lead to incoherent relations between the results; trial and error concluded that the best results are obtained when the two surfaces where the wires are attached are coated with silver paint to serve as an even distribution for the disk; this warranties that both sides have exactly the same diameter therefore equal surface area.

The pellets were prepared on a manual hydraulic press

3.4.4 – Impedance Spectroscopy Measurements and Conditions

Pellets were prepared as samples for measuring proton conductivity for all doping ratios of the system of Rb_xCs_{1-x}H_2PO_4. The impedance spectroscopy measurements were performed using a Solartron 1260 impedance analyzer coupled with a ProboStat® sample holder. A 100 mV oscillating potential in a frequency range from 6 MHz to 1 Hz was applied in a standard two-point, four-wire setup.
The pellets were previously coated in both faces with silver paste so that a uniform and consistent electrode surface area was obtained; platinum wires were used as measurement leads. For temperature measurements the sample holder (ProboStat) was placed inside a vertical tube furnace, where there was full control of the temperature ramp rate and the time spent in each temperature; the temperature varied within the 160 – 250°C range. In conductivity was determined from Nyquist plots.

3.4.5 – Impedance Spectroscopy Data and Interpretation

Data was obtained from a Cole-Cole Plot and using the relation separated between the real and imaginary parts. Then explain Cole-Cole plots with images and how it relates to super protonic behavior. Where the Bulk resistance of the electrolyte is the diameter of the semicircle but if we have super protonic behavior we do not see a semicircle because the conductivity is too large and we only measure from the origin to the plot.

\[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + (i\omega\tau_0)^{1-\alpha}} \]

Equation 4: Cole – Cole Equation

Bode plots present the data in as the system responds to frequency; they are presented usually as a combination of a Bode magnitude plot, (the magnitude of the frequency response in decibels) and a Bode phase plot (the phase shift). Both quantities are then plotted with a horizontal axis proportional to the logarithm frequency. Simple method for graphing gain and phase-shift plots, maintaining stability and taking in consideration the variations in circuit characteristics originated by the bad calibration of the product or errors during the measurement collection.

Nyquist plot allows a representation easy to understand for a frequency response system. In Cartesian coordinates, the real part of the transfer function is plotted on the X-axis and the imaginary part on the Y-axis. In polar coordinates, the gain of the transfer function is plotted as
the radial coordinate, while the phase of the transfer function is plotted as the angular one. This form can provide more information about the shape of the transfer function; for example, the angle at which the curve approaches the origin can give us information about the number of poles and zeros of the function.

Both engineers that came up with these two representation methods (Bode and Nyquist) used to work at Bell Laboratories.

**Figure 10:** The impedance data are the black points, the projection onto the $Z'' - Z'$ plane is called the Nyquist plot.

A final detail to remember is that the impedance of the system is represented by a complex number which specific representation within the complex plane with the Y-axis been imaginary
and the X-axis real; each data point represents a different frequency, the impedance is then represented as a vector of length $|Z|$ with an angle between it and the x-axis given by $\varnothing$.

Afterwards we can then do the calculations for the conductivity of the material based on the point of lowest frequency that touches the x-axis using a simple relation (Figure 10).

Using the Equation 5 and the previously explained method of data acquisition we are able to determine the conductivity of the material manually, of course we have a software that takes care of this calculations when the system becomes too complicated for the manual analysis: ZMan 2.3 software.

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

**Equation 5**: Conductivity calculation from the Nyquist plot; $A$ is the area of the electrodes, $l$ is the separation between electrodes, and $R$ is the resistance in contact with the x-axis at the end of the semicircle (lowest frequency).

Diffusion from other elements can cause an impedance known as Warburg impedance which depends on the frequency of the potential perturbation. In a Nyquist plot, the Warburg impedance appears as a diagonal line with slope of $0.5$ in a Bode plot, the Warburg impedance exhibits a phase shift of $45^\circ$. $^{51}$
Chapter 4: Experimental Results

The Chapter we will show that the synthesis process was successful and that we obtained the desired mixed-metal solid acid materials. We show this through the results of two experiments, EDS, and SCXRD. Next, we will show the structural dependence on x with SCXRD and how the symmetry and crystal phase is affected. Then we will demonstrate how these changes affect proton conductivity within the materials using Impedance Spectroscopy. Lastly, we will demonstrate how a known change in phase from tetragonal to monoclinic is affected by doping changing the temperature of transition.

4.1 – EDS

First, we used two independent techniques, EDS and SC-XRD, to determine the actual Rb-doping level, x, in the mixed Rb_xCs_{1-x}H_2PO_4 (0 < x < 1) series. This initial characterization is of particular importance, as validating the values of x predicted from synthesis defines the overall accuracy of our study.

![Figure 11: EDS data and corresponding SEM images (inset) collected on an Rb_{0.2}Cs_{0.8}H_2PO_4 sample allow accurate elemental analysis that confirms the metal ratio sought in synthesis and independently obtained from X-ray analysis via structure refinement.](image)

Figure 11: EDS data and corresponding SEM images (inset) collected on an Rb_{0.2}Cs_{0.8}H_2PO_4 sample allow accurate elemental analysis that confirms the metal ratio sought in synthesis and independently obtained from X-ray analysis via structure refinement.
Figure 11 shows the EDS results for the Rb$_{0.2}$Cs$_{0.8}$H$_2$PO$_4$ sample. The spectrum, collected within the 0 - 14.25 keV energy range upon focusing the electron beam onto a small area of the sample (inset), shows robust peaks characteristic for Cs and Rb. Quantitative analysis based on their relative intensities allowed us to experimentally determine the Rb-doping level: we found $x_{\text{exp}} = 0.195$ a value very close to its calculated (from synthesis) counterpart, $x_{\text{calc}} = 0.2$. We carried out similar EDS measurements and analyses for all the other mixed compounds in series ($0 < x < 1$) and, in each case, determined the experimental Rb-doping level.

Figure 12, shows the values of the experimentally determined Rb-doping level $x_{\text{exp}}$ from EDS (filled circles) and XRD (empty circles) as a function of their synthesis-predicted counterpart $x_{\text{calc}}$. 
Figure 12: Comparison between the Rb-doping levels expected from synthesis in the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ ($0 \leq x \leq 1$) series $x_{\text{calc}}$ and its experimental counterparts $x_{\text{exp}}$ measured from EDS (triangles) and SC-XRD (circles).

4.2 – SCXRD Characterization

We then determined $x_{\text{exp}}$ using SC-XRD. Briefly, this was done by refining the substitutional disorder at the site of the Rb/Cs metal centers against Fourier difference maps calculated from data collected on each member of the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ ($0 < x < 1$) series. ‘PART’ commands and a free variable were used to determine the weighted average of the two metals that best matches the electron density seen in the Fourier difference maps.$^{52}$

Next, the crystal structures of the mixed solid acids Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ were determined from SC-XRD experiments for $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$, and 1. The crystallographic results of these experiments are summarized in Table 3.
Table 3: Crystallographic data on the Rb<sub>x</sub>Cs<sub>1-x</sub>H<sub>2</sub>PO<sub>4</sub> (0 ≤ x ≤ 1) series obtained from single crystal data analysis

<table>
<thead>
<tr>
<th>Cation ratio</th>
<th>C&lt;sub&gt;Rb&lt;/sub&gt;</th>
<th>C&lt;sub&gt;Rb&lt;/sub&gt;</th>
<th>C&lt;sub&gt;Rb&lt;/sub&gt;</th>
<th>C&lt;sub&gt;Rb&lt;/sub&gt;</th>
<th>C&lt;sub&gt;Rb&lt;/sub&gt;</th>
<th>C&lt;sub&gt;Rb&lt;/sub&gt;</th>
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<th>C&lt;sub&gt;Rb&lt;/sub&gt;</th>
</tr>
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<tbody>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>I - 42d</td>
<td>P 2(1)/c</td>
<td>P 2(1)/m</td>
<td>P 2(1)/m</td>
<td>P 2(1)/m</td>
<td>P 2(1)/m</td>
<td>P 2(1)/m</td>
<td>P 2(1)/m</td>
</tr>
<tr>
<td>T (K)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
</tr>
<tr>
<td>Unit cell dimensions (Å, °)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>7.6067(3)</td>
<td>9.5663(5)</td>
<td>4.8283(3)</td>
<td>4.8415(3)</td>
<td>4.8504(3)</td>
<td>4.8600(3)</td>
<td>4.8728(2)</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>7.6067(3)</td>
<td>6.2161(4)</td>
<td>4.8283(3)</td>
<td>4.8415(3)</td>
<td>4.8504(3)</td>
<td>4.8600(3)</td>
<td>4.8728(2)</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>7.7067(4)</td>
<td>7.6689(6)</td>
<td>7.7772(5)</td>
<td>7.8076(5)</td>
<td>7.8276(4)</td>
<td>7.8476(4)</td>
<td>7.8894(4)</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td></td>
</tr>
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<td>β</td>
<td>90</td>
<td>108.852(2)</td>
<td>108.024(2)</td>
<td>108.01(1)</td>
<td>107.879(2)</td>
<td>107.739(2)</td>
<td>107.739(2)</td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Volume (Å&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>422.06(4)</td>
<td>433.70(4)</td>
<td>218.35(3)</td>
<td>223.76(2)</td>
<td>224.63(2)</td>
<td>226.74(2)</td>
<td>228.66(2)</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Calculated density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>4.963</td>
<td>4.830</td>
<td>4.681</td>
<td>4.619</td>
<td>4.580</td>
<td>4.529</td>
<td>4.485</td>
<td></td>
</tr>
<tr>
<td>Absorption coefficient (mm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>20.491</td>
<td>19.941</td>
<td>19.805</td>
<td>19.326</td>
<td>11.718</td>
<td>19.071</td>
<td>18.911</td>
<td></td>
</tr>
<tr>
<td>2θ range</td>
<td>7.576 to 56.41°</td>
<td>5.586 to 62.01°</td>
<td>5.58 to 56.64 °</td>
<td>8.521 to 54.37°</td>
<td>6.48 to 61.30°</td>
<td>8.44 to 61.2°</td>
<td>6.41 to 56.63°</td>
<td></td>
</tr>
<tr>
<td>Unique reflections</td>
<td>265</td>
<td>1452</td>
<td>598</td>
<td>539</td>
<td>747</td>
<td>745</td>
<td>757</td>
<td></td>
</tr>
<tr>
<td>Total reflections</td>
<td>3632</td>
<td>10419</td>
<td>10836</td>
<td>5586</td>
<td>11284</td>
<td>8448</td>
<td>8604</td>
<td></td>
</tr>
</tbody>
</table>

It's noteworthy that the crystal structure of the undoped compound (x = 0) – monoclinic P<sub>2</sub>/m – persists upon increasing the Rb content up to x = 0.7 (Rb<sub>0.7</sub>Cs<sub>0.3</sub>H<sub>2</sub>PO<sub>4</sub>). Further doping to x = 0.8, however, results in several structural changes.

Indeed, for Rb<sub>0.8</sub>Cs<sub>0.2</sub>H<sub>2</sub>PO<sub>4</sub> the mirror plane is lost, the unit cell doubles in size along the a-axis, and the space group changes over to P<sub>2</sub>/c. In addition, the number of formula units in the cell, Z, increases from 2 to 4. Upon increasing the doping level to x = 0.9, the crystal symmetry...
changes again from monoclinic to tetragonal (I-42d). As shown by the results in Table 4, the tetragonal crystal structure of Rb\textsubscript{0.9}Cs\textsubscript{0.1}H\textsubscript{2}PO\textsubscript{4} is isomorphic with that of pure RbH\textsubscript{2}PO\textsubscript{4}, a similar behavior to the one exhibited at the other end of the series, where an isomorphism relation exists between monoclinic Rb\textsubscript{0.1}Cs\textsubscript{0.2}H\textsubscript{2}PO\textsubscript{4} and CsH\textsubscript{2}PO\textsubscript{4}.

**Table 4:** Comparison between the crystallographic data of the room temperature phases of CDP and RDP and those of the mixed solid acids Rb\textsubscript{0.1}Cs\textsubscript{0.9}H\textsubscript{2}PO\textsubscript{4} (x = 0.1) and Rb\textsubscript{0.9}Cs\textsubscript{0.1}H\textsubscript{2}PO\textsubscript{4} (x = 0.9), respectively

<table>
<thead>
<tr>
<th>Unit cell dimensions (Å, °)</th>
<th>CDP</th>
<th>Cs0.9Rb0.1H2PO4</th>
<th>RDP</th>
<th>Cs0.1Rb0.9H2PO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4.880(1)</td>
<td>4.8728(2)</td>
<td>7.607</td>
<td>7.6067(3)</td>
</tr>
<tr>
<td>b</td>
<td>6.383(1)</td>
<td>6.3776(3)</td>
<td>7.607</td>
<td>7.6067(3)</td>
</tr>
<tr>
<td>c</td>
<td>7.912(2)</td>
<td>7.8894(4)</td>
<td>7.299</td>
<td>7.2942(3)</td>
</tr>
<tr>
<td>α</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β</td>
<td>107.73(2)</td>
<td>107.739(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å\textsuperscript{3})</td>
<td>234.74(1)</td>
<td>233.52(2)</td>
<td>422.9(4)</td>
<td>422.06(4)</td>
</tr>
</tbody>
</table>

**Figure 13:** Unit cells and corresponding diffraction patterns of the three types of crystal structures that occur in the Rb\textsubscript{x}Cs\textsubscript{1-x}H\textsubscript{2}PO\textsubscript{4} (0 ≤ x ≤ 1) series upon the increase of the Rb doping level x: left: monoclinic P2\textsubscript{1}/m for values of x from 0 to 0.6; center: monoclinic P2\textsubscript{1}/c for x = 0.8, right: tetragonal I-42d for x = 0.9.

The variation of the unit cell parameters (a, b, c, β) and volume (V) upon increasing the Rb-doping level (x) determined from SC-XRD measurements are shown in Figure 11. Here, we first note that the length of all three unit-cell axes decreases monotonically with increasing x.
within the monoclinic P21/m (0 ≤ x ≤ 0.7) range, an expected behavior as smaller Rb atoms (ionic radius 166 pm)\textsuperscript{55} progressively replace their larger Cs counterparts (ionic radius 181pm).\textsuperscript{55}

Figure 14: Unit cell parameters as a function of the Rb-doping level x in the three crystallographic phases present upon increasing x in the Rb\textsubscript{x}Cs\textsubscript{1-x}H\textsubscript{2}PO\textsubscript{4} (0 ≤ x ≤ 1) series.

The unit cell volume V decreases with the amount of rubidium linearly, in accordance with Vegard's law.\textsuperscript{56} Another observation is that the monoclinic symmetry persists at x = 0.8, but the space group changes from P21/m to P21/c as a result of the loss of the mirror plane. In addition, axis a doubles in length-- with respect to the value expected if the decrease of this unit cell parameter had continued to x = 0.8 – while the other two axes, b and c, remain comparable to their
x = 0.7 values and do continue their decrease. In addition, the unit-cell volume of the x = 0.8 compound reaches ~434 Å³ (compared to its x = 0.7 counterpart ~218 Å³) and the number of formula units in the unit cell doubles from 2 to 4.

This is the first observation of a P21/c structure within the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ (0 ≤ x ≤ 1) series. Previously reported were the monoclinic P2$_1$/m and tetragonal I-42d modifications (which belong to the two ends x = 0 and x = 1, respectively). In this respect, our results our results differ from a recent powder diffraction study by Martsinkevich et al.\textsuperscript{31}, where a P2$_1$/m space group was reported to persist throughout the entire range of x studied.

Another interesting aspect of the P21/c crystal structure of Rb$_{0.8}$Cs$_{0.2}$H$_2$PO$_4$ is the fact that the PO$_4$ tetrahedra are disordered. In fact, this appears to be the reason for the above-mentioned symmetry break: the mirror plan (in the P2$_1$/m structure) bisects the PO$_4$ tetrahedra, and, as they become disordered, the mirror is lost. Moreover, this newly uncovered structure might be significant, as several studies have indicated that tetrahedral disorder is directly linked to proton conductivity enhancement in solid acid materials, particularly in CsH$_2$PO$_4$.\textsuperscript{17}

However, the disorder in Rb$_{0.8}$Cs$_{0.2}$H$_2$PO$_4$ appears not to be rotational (as in the high temperature superprotonic CsH$_2$PO$_4$ phase), but substitutional, where the positions of the tetrahedral centers in the unit cell are determined by the Rb/Cs ratio. It is therefore important to carry out impedance spectroscopy measurements on low and high Rb-doping level members of the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ series in order to clarify the effects of the observed microscopic structural changes, including PO$_4$ disorder, on the macroscopic proton conductivity of these mixed compounds.
4.3 – Impedance Spectroscopy

As for the impedance spectroscopy measurements, it was necessary to press the fine powder into a pellet of small diameter and thickness for calculations of conductivity, as a known separation between the electrodes is required.

The pellet preparation took place on a manual hydraulic press capable of reaching 25,000 pounds of pressure, after several trials with the pressure and sample quantity it was determined that applying 18,000 psi for 1 minute and then a slow release was the most effective way to obtain almost identical pellets with equal diameter of 10.23 mm but a slightly different thickness where the average was 2.68 mm ±.12 depending mostly on the doping ratios which changed the density of the material resulting in thicker pellets.

![Pressed pellet of CDP at 18,000 pounds. To the left we have the pellet by itself and to the right a layer of silver paste on both faces of it.]

Figure 15: Pressed pellet of CDP at 18,000 pounds. To the left we have the pellet by itself and to the right a layer of silver paste on both faces of it.

The pellets where then measured and painted for the analysis, with a uniform layer of silver paste on both sides that will act as electrodes directly attached to the sample that then will be placed in the spring loaded mechanism of our sample holder.
**Figure 16**: The image on the top is the side to side some of the electrodes used in the studies; underneath we have the loaded sample between the two electrodes.

In Figure 16 we can see the two electrodes on top with the assembled sample holder on the bottom, the spring loaded mechanism is also attached, from here we only need to place the protective cover and loaded into the vertical tube furnace.

Figure 17 shows Nyquist plots (out-of-phase impedance $Z''$ vs. its in-phase counterpart $Z'$) measured on Rb$_{0.1}$Cs$_{0.9}$H$_2$PO$_4$ (x = 0.1) at different temperatures, T, within the 190°C – 245°C range. The upper panel (a) shows data collected at lower temperatures T = 190°C (squares), T = 220°C (circles) and T = 225°C (triangles).

In all the cases the Nyquist behavior measured at frequencies between $10^6$ Hz and $10^3$ Hz exhibits a semicircle shape. The intersection of each semicircle with the $Z'$ axis (at low frequencies) and size of the cylindrical sample (pellet) used in these impedance spectroscopy
experiments can be used to determine the proton conductivity $\sigma$ at that temperature $^{57, 51}$. This analysis shows that the proton conductivity of Rb$_{0.1}$Cs$_{0.9}$H$_2$PO$_4$ changes little upon heating from 190$^\circ$C to 225$^\circ$C, having values $\sigma \sim 5 \times 10^{-6}$ S cm$^{-1}$. This behavior and the measured values of $\sigma$ are similar to those previously observed in the monoclinic CsH$_2$PO$_4$ phase $^{58}$.

The lower panel (b) shows the Nyquist plots recorded on the same compound Rb$_{0.1}$Cs$_{0.9}$H$_2$PO$_4$, but at higher temperatures $T = 235^\circ$C (squares), $T = 240^\circ$C (circles) and $T = 245^\circ$C (triangles) upon varying the measurement frequency between $10^6$ Hz and 1 Hz. Here $Z''$ vs. $Z'$ exhibits a behavior markedly different from the semicircles observed at lower temperatures.

Moreover, the proton conductivity - determined from the intersection of the linear segment of the Nyquist plots with the $Z'$ axis $^{57}$ – has values *three orders of magnitude greater* than the ones measured at temperatures below 230$^\circ$C. At $T = 245^\circ$C, for example, $\sigma = 4.1 \times 10^{-3}$ S cm$^{-1}$.

This dramatic increase in proton conductivity upon heating above a temperature threshold (superprotonic behavior) is most likely due to the same monoclinic-to-cubic polymorphic phase transition as the one observed in the undoped compound CsH$_2$PO$_4$ $^{58}$.

We have carried out similar measurements and analyses on the other members of the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ series and found that the behavior showed in Fig. 17 (a) and (b) persists up to Rb-doping levels of $x = 0.7$. 
Figure 17: Nyquist plots (out-of-phase $Z''$ vs. in-phase $Z'$ impedance) collected on Rb$_{0.1}$Cs$_{0.9}$H$_2$PO$_4$ ($x = 0.1$) at (a) $T = 200^\circ$C (squares), $T = 220^\circ$C (triangles), $T = 230^\circ$C (circles) and at (b) $T = 235^\circ$C (squares), $T = 240^\circ$C (circles), $T = 245^\circ$C (triangles).

This is consistent with the fact that the crystal structure of Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ has the same symmetry and space group (monoclinic P2$_1$/m) for all Rb-doping values between $x = 0$ (undoped CsH$_2$PO$_4$) and $x = 0.7$. As demonstrated by our SC-XRD results discussed above further increasing $x$ to 0.8 results in a crystal structure change. Indeed, for Rb$_{0.8}$Cs$_{0.2}$H$_2$PO$_4$ the mirror plane is lost,
the unit cell doubles in size along the a-axis, and the space group changes over to P21/c. In addition, the number of formula units in the cell, Z, increases from 2 to 4, and, very importantly, PO₄ tetrahedral disorder is present. All these structural changes (with respect to the compounds where \( x \leq 0.7 \)) have a strong effect on the proton conductivity of Rb₀.₈Cs₀.₂H₂PO₄ (\( x = 0.8 \)).

As shown in Figure 18, the Nyquist plots collected at temperatures between 180°C and 240°C exhibit the same qualitative behavior throughout the entire temperature range, with no major changes observed upon heating above 230°C (as was the case for \( x \leq 0.7 \), see Figure 5). This indicates that no abrupt jump in the proton conductivity (superprotonic behavior) is observed in Rb₀.₈Cs₀.₂H₂PO₄.

![Figure 18](image_url)

**Figure 18:** Temperature resolved Nyquist plots collected on Rb₀.₈Cs₀.₂H₂PO₄ (\( x = 0.8 \)) at \( T = 180^\circ\text{C} \) (squares), \( T = 220^\circ\text{C} \) (circles), \( T = 230^\circ\text{C} \) (upright triangles), \( T = 235^\circ\text{C} \) (inverted triangles), and \( T = 245^\circ\text{C} \) (diamonds).
Figure 19 shows the proton conductivity, $\sigma$ measured at temperatures between 180°C and 250°C on the $x = 0.1$ (triangles), $x = 0.8$ (circles) and $x = 0.9$ (squares) compounds.

The data confirms that a superprotonic behavior is present in the $x = 0.1$ sample, but not in $x = 0.8$ or 0.9. In addition, the proton conductivity of the high Rb-doping level compounds, $x = 0.8$ and 0.9, measured at temperatures below 230°C is nearly two orders of magnitude higher than that of their $x = 0.1$ counterparts. Interestingly, however, further heating (above 230°C) leads to values of $\sigma$ that are lower for the $x = 0.8$ and 0.9 samples than those recorded on the lightly Rb-doped compound ($x = 0.1$). At 250°C, for example, $\sigma \sim 2 \times 10^{-3}$ S·cm$^{-1}$ for $x = 0.8$, whereas $\sigma \sim 4.8 \times 10^{-3}$ S·cm$^{-1}$ for $x = 0.1$. Therefore, there are two conclusions from the data presented in Figure 19.
First, these results demonstrate that high levels of Rb-doping (x > 0.7) lead to a significant enhancement of the proton conductivity of CsH₂PO₄ at temperatures below its superprotonic transition. But still, at temperatures above the transition, the lower Rb-doping compounds exhibit a higher conductivity.

This is shown in Figure 20, where the proton conductivity of RbₓCs₁₋ₓH₂PO₄ (determined at T = 240°C from Nyquist plots as the ones in Figures 17 and 18) is plotted vs. the Rb-doping level x. The conductivity decreases with increasing x from 5.2×10⁻³ S·cm⁻¹ for the undoped (x = 0) compound CsH₂PO₄ to 8×10⁻¹ S·cm⁻¹ for Rb₀.₉Cs₀.₁H₂PO₄, x = (0.9).

Figure 20: Variation of the proton conductivity, σ with the Rb-doping level, x, measured at T = 240°C
Figure 21: SCXRD of Rubidium Dihydrogen Phosphate at its transition temperatures were we go from a tetragonal structure to a monoclinic at about 120 °C; this new monoclinic structure is identical of that of room temperature Cesium Dihydrogen Phosphate.

As indicated above, the monoclinic symmetry persists in Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ upon the increase of $x$ from 0 to 0.8. At $x = 0.9$ the symmetry changes to tetragonal, space group I -4 2 d. The corresponding crystal structure of Rb$_{0.8}$Cs$_{0.2}$H$_2$PO$_4$ has 4 formula units in the unit cell ($Z = 4$) and is isomorphic (crystallographic ally identical) to that of the “fully-doped” RbH$_2$PO$_4$ ($x = 1$). It is known that the tetragonal RbH$_2$PO$_4$ phase changes to monoclinic P2$_1$/m upon heating above 120°C, and, remarkably, this intermediate-temperature monoclinic RbH$_2$PO$_4$ phase is isomorphic with the room-temperature CsH$_2$PO$_4$.

The superprotonic behavior of CsH$_2$PO$_4$ is known to be associated with a (P2$_1$/m) → (Pm3m) polymorphic transition at T~233°C $^{17,18}$, and there is preliminary evidence that the same monoclinic → cubic transition is responsible for the superprotonic behavior of RbH$_2$PO$_4$ but at a much higher temperature ~295°C. It is therefore interesting to investigate if mixed-cation compounds Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ with high Rb-doping levels ($x = 0.9$) exhibit a different behavior in terms of the transition temperatures upon heating the RT tetragonal phase. Figure 21 shows SCXRD data that evidence the tetragonal (I-42d) → monoclinic (P 2$_1$/m) transition in RbH$_2$PO$_4$, with
corresponding unit cells shown as insets. As expected [1] the transition occurs at T~120°C. For the mixed compound (Rb0.9Cs0.1H2PO4), however, the same transition is observed at a significantly lower temperature, T~80°C. This is a remarkable behavior and, to the best of our knowledge, it represents the first observation of a dramatic change (by 33%) of polymorphic transition temperatures in phosphate-based solid acids by cation doping.

Figure 22: SCXRD of Rubidium- Doped Cesium Dihydrogen Phosphate at the highest doping end, x = 0.9, were the same phase transition occurs as shown in figure 21 but at a lower temperature, around 80°C.

This is also important, as the ability to tune the structural transition temperatures of these systems can be potentially used to control the temperature behavior of their proton conductivity and therefore their functionality as fuel cell electrolytes. As a next step, we plan to carry a more extensive investigation into the effect of having mixed cations on the monoclinic → cubic superprotonic transition in Rb0.1Cs0.9H2PO4 and Rb0.9Cs0.1H2PO4. These experiments are currently under way.
Chapter 5: Conclusion

A range of materials of the type RbxCs1-xH2PO4 (0 ≤ x ≤ 1) were synthesized effectively every time following the same procedure and stoichiometry, from which both single crystal samples and after complete drying powder samples were grinded with pestle and mortar.

SCXRD Crystals suitable for analysis that were grown via wet slow precipitation were accurately refined with the procedures described in above sections to find their structures; these structures are reported within ACTA crystallographic information files (.cif), these files serve the purpose of supplying the additional information for the accurate completion of the structures.

SCXRD + EDS from the Fourier difference map the ratio of metals was determined and confirmed by EDS measurement. At high levels of x symmetry changed. We have investigated the structural modifications that occur upon Rb-doping of the superprotonic conductor CsH2PO4.

We used single crystal x-ray diffraction to accurately determine the crystal structures of the RbxCs1-xH2PO4 (0 ≤ x ≤ 1) series, we found that the monoclinic P21/m modification belonging to the parent compound CsH2PO4 persists upon the increase of the Rb-doping level form x = 0.1 to x = 0.7. Further doping to x = 0.8 results in a symmetry change to a previously unreported monoclinic P21/c phase, where the mirror plane is lost and disorder is present in the PO4 tetrahedra even at room temperature.

Temperature-resolved ac impedance spectroscopy to measure the proton conductivity of these compounds at different values of the Rb-doping, x; correspondingly, a superprotonic behavior (there orders of magnitude jump in the proton conductivity, σ, upon heating above 230°C) occurs in compounds where x≤0.7, while a gradual increase of σ is observed for x≥0.8. At x = 0.9 the crystal structure changes to tetragonal I-42d modification isomorphic with the room temperature structure of RbH2PO4.
Our impedance spectroscopy data also revealed that $\sigma$ measured at 240°C increases with the decrease of $x$, so the most proton conductor at this temperature is still CsH$_2$PO$_4$. At lower temperatures (below 230°C), however, $\sigma$ is two orders of magnitude higher at high values of $x$ ($\geq 0.8$).

Finally, we demonstrated for the first time that the tetragonal-to-monoclinic polymorphic phase transition temperature has a strong dependence on $x$: it changes from 120°C to 80°C. This indicates an effect of the critical temperature for polymorphism from the metal ratio chosen. The ability to affect the critical temperature for phase transformations is crucial, as both mechanical integrity and decomposition rate are affected by increased temperature.
References


[14] High-temperature crystal structures and chemical modifications in RbH2PO4,RJ Tackett, H,Martinez, RR Chianelli, J Zhang, Y Zhao, CE Botez,APS Meeting Abstracts 1, 38011


[38] SAINT Version 7.68a, Bruker AXS Inc.; Madison, WI 2009.


Curriculum Vita

Andres Jose Encerrado Manriquez was born in Cd. Juarez, Chihuahua, Mexico, on November of 1992. After finishing high school in 2010 back in Mexico, he joined the University of Texas at El Paso under a degree in Mathematics which latter changed to Physics. Here he worked as an undergraduate as a Teacher Assistant for a variety of classes, workshops and laboratories in Physics topics, as well as a Undergraduate Research Assistant for the X-Ray Scattering Laboratory under the supervision of Dr. Cristian E. Botez.

In the research he was able to collaborate with other students and researchers through the university which made him an awardee of the COURI program for scientific contributions during the undergraduate studies in 2012. He received his Bachelor’s degree in Applied Physics late in 2014 and joined the graduate program in Physics the following term.

After been mentor for undergraduate students, participant in many international conferences, teacher assistant for advance laboratories in physics and part of the research team leader in collaborations across disciplines on the department he completed his Master’s degree in Physics on May 2017.

Structural modifications in the Rb_xCs_{1-x}H_2PO_4 (0≤x≤1) superprotonic conductor series: a single crystal X-ray Diffraction and Impedance Spectroscopy study. This work is part of an ongoing effort across fields by the department of defense to find and test new electrolyte materials for fuel cell applications to surpass the current limits of the industry.
CAREER SUMMARY
Worked in a team environment doing research in the X-ray Scattering Laboratory under the supervision of Dr. Cristian Botez synthesizing, preparing and analyzing samples for our research on Solid Acid Electrolytes as well as many collaborations with other university research groups. Managed physics and math oriented workshops, laboratories and tutor sessions; assisted in the recruitment events on high schools and inside the university for the department of physics.

EDUCATION

Jan 2015 – May 2017 The University of Texas at El Paso El Paso, TX
Masters of Science (M.S.) in Physics
Thesis: Structural modifications in the $\text{Rb}_x\text{Cs}_{1-x}\text{H}_2\text{PO}_4$ ($0 \leq x \leq 1$) superprotonic conductor series: a single crystal X-ray Diffraction and Impedance Spectroscopy study.
- Cumulative GPA: 3.30/4.0

Aug 2010 – Dec 2014 The University of Texas at El Paso El Paso, TX
Bachelor of Science (B.S.) in Physics
- Cumulative GPA: 3.04/4.0

EXPERIENCE

Jan 2011 – May 2017 The University of Texas at El Paso X-Ray Scattering Lab
Graduate and Undergraduate Research Assistant
Project: Electrochemical Impedance Spectroscopy: A Study on Phosphate Based Solid Acid Salts
- In collaboration with X-Ray Scattering Lab and the Department of Defense, designed and executed experimental project to analyze the properties of Cesium Dihydrogen Phosphate (CDP).
- Analyzed collected data with XRD and AC Impedance Spectroscopy.

Project: Chemical and Physical Characteristics of Bismuth Ferrite
- Designed experimental processes to detect phase transformations in Bismuth Ferrite through direct thermal decomposition synthesis with XRD data collection and analysis.

Project: Structural and Chemical Behavior Analysis of a Local Crystalline Formation: Desert Rose
- Analyzed sample composition of Desert Rose crystalline formation collected from the Desert of Chihuahua.
• Replicated the found compound through the supersaturation-controlled synthesis technique in a controlled research environment with the purpose of implementing it in the removal of heavy compounds in polluted water.

Project: Conditions Dependence Crystallite Phases on Doped Phosphate Salts
• In collaborative effort with the X-Ray Scattering team, designed an experimental process that tested and analyzed the characteristics of doped phosphate salts for fuel cell applications.

Project: Chemical Transformations of Acetaminophens
• Trained and supervised a research team of 4 undergraduate students on methods of sample preparation, and data collection and analysis with a powder diffractometer.

Project: Structural Temperature Dependence of Potassium and Rubidium Phosphate Salts
• Assisted in a collaborative effort between the X-Ray Scattering team and the Department of Defense with sample preparation and data collection and analysis.

Jan 2011 – May 2017 The University of Texas at El Paso X-Ray Scattering Lab

Graduate and Undergraduate Teaching Assistant
• Supervised processes for advanced Physics laboratories in circuits and mechanics.
• Conducted Physics workshops and tutoring sessions for a total of 520 undergraduate students of various career fields.
• Conducted regular maintenance checks on laboratory equipment to include cleaning and storage.
• Trained new Teacher Assistants on proper equipment use and maintenance.
• Graded and provided feedback to students on their progress throughout the semester.

SKILLS

Interpersonal
• Excellent interpersonal communication skills. Fluent in English and Spanish, written and oral expression.
• Able to work as part of a team and take leadership positions when necessary.
• Capable of dealing with stressful situations while dealing with others.
• Group

Research Software

Instrumentation
• Trained in the operation, maintenance, and troubleshooting of single crystal and powder diffraction machinery and software: Bruker’s Siemens D5000 and D8 Discover, Panalytical’s Empyrean.
• Assembly and operation of ProboStat for non-ambient impedance spectroscopy.
• Competent user of Multimeters, Oscilloscopes and Power Sources.
• Able to assemble simple circuitry and soldering.

Programming and Scripting
• C++, Fortran, Python.

Languages
• Fluent communication in Spanish and English.

PUBLICATIONS

Journals

*Monoclinic RbD$_2$PO$_4$: Room temperature synthesis, chemical and structural stability upon heating, Elsevier, vol. 143, no.2, pp 605-610, Jan 2014*

- Cristian E. Botez, Masoud Mollaee, Andres J. Encerrado Manriquez, Michael P. Eastman.

*Heating induced structural and chemical behavior of KD$_2$PO$_4$ in the 25°C – 215°C temperature range, Elsevier, vol. 83, pp. 74-78, Sep 2013*

- Cristian E. Botez, Joshua L. Morris, Andres J. Encerrado Manriquez, Adan Anchondo.

Conferences

*Structural modifications in the Rb$_x$Cs$_{1-x}$H$_2$PO$_4$ (0≤x≤1) superprotonic conductor series: a single-crystal x-ray diffraction and impedance spectroscopy study.*

- Conference: Spring 2017 Meeting of the Texas Sections of APS, Texas Section of AAPT, and Zone 13 of the Society of Physics Students at San Antonio, Texas, USA, March 2017.

*Conductivity of Cs$_{1-x}$SiO$_2$H$_2$PO$_4$ though Impedance Spectroscopy: Temperature Dependence Study.*


*Study of naturally grown Desert Rose formations from the Chihuahua Desert: A structural and chemical behavior analysis.*


*Monoclinic RbD$_2$PO$_4$: room temperature synthesis, chemical and structural stability upon heating.*

- Collaboration: Cristian E. Botez, Masoud Mollaee, Andres J. Encerrado Manriquez, Michael Eastman.
- Conference: Joint Fall 2013 Meeting of the Texas Sections of the APS, AAPT, and Zone 13 of the SPS, Volume 58, Number 10 at Brownsville, Texas, USA, Oct 2013.

*X-ray Diffraction Study of Acetaminophen.*

- Conference: Joint Fall 2013 Meeting of the Texas Sections of the APS, AAPT, and Zone 13 of the SPS, Volume 58, Number 10 at Brownsville, Texas, USA, Oct 2013.

*Heating Induced structural and chemical behavior of KD$_2$PO$_4$ in the 25°C-215°C temperature range.*


_Heating Induced structural and chemical behavior of KD₂PO₄ in the 25°C-215°C temperature range._


• Conference: Joint Spring 2013 Meeting of the Texas Sections of the APS, AAPT, and Zone 13 of the SPS, Volume 58, Number 3 at Tarleton, Texas, USA, Apr 2013.

**AFFILIATIONS AND ACTIVITIES**

**Professional**

*American Chemical Society (ACS)*

Member, 2011 – Present

*American Crystallographic Association (ACA)*

Member, 2013 – Present

*Society of Physics Students (SPS)*

Member, 2011 – Present

**In Campus**

*Club Zero*

Member, 2011 – 2014

SPS UTEP branch

Member 2011 – 2014

**ACADEMIC HONORS AND AWARDS**

*Travel Grant, ACA.*

Awarded to a select group of attendees of the annual meeting, Jul 2015.

*Travel Grant, UTEP Graduate School.*

Awarded to graduate students with research of interest, Jul 2015.

*COURI Award, UTEP Undergraduate Research Program.*

For scientific contributions during the undergraduate studies, Campus Program, Aug 2012.

*Benito Juarez Award, Liberty Partnership Program at St. John’s University.*

Providing sponsorship with stipend for undergraduate studies on the field of science, Jan 2011.

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This thesis/dissertation was typed by < Andrés José Encerrado Manriquez>.