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RPPR Final Report
as of 27-Dec-2018

Agency Code:

Proposal Number: 67290CHREP **Agreement Number: W911NF-15-1-0494**

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STEM Degrees: 10 **STEM Participants:** 15

Major Goals: The main research goal of our project is to stabilize the superprotonic phase of CDP (and/or other phosphate-based solid acids) without the use of high-pressure or high-humidity conditions. Achieving this goal represents a critical step towards the large-scale use of these materials as intermediate temperature fuel cell electrolytes. This is due to the fact that the instability (dehydration) of the superprotonic phases under ambient pressure and humidity is the main barrier to progress towards the above mentioned application.

A first major goal within our proposed approach is to determine the microscopic (crystal structure) and macroscopic (proton conductivity) modifications that accompany the dehydration and chemical decomposition of the superprotonic phases of phosphate solid acids. A second goal is synthesize composite materials based on phosphate solid acids and highly dispersed oxides, and to investigate the crystal structures, proton conduction mechanisms, and thermal stability of their superprotonic phases.

The main instructional goal of our project is to attract and retain underrepresented minority students to work on this project and provide them with outstanding research and instruction opportunities needed to complete advanced degrees (M.S. and Ph.D.) and successfully compete for employment in STEM disciplines.

Besides its fundamental-science impact, our proposed research has the potential to address a critical technological issue for the field of intermediate-temperature fuel cells, namely the instability of the superprotonic phases of phosphate solid acids under ambient pressure and humidity conditions. Indeed, stabilizing these phases will likely lead to the large-scale use of the proposed materials as novel intermediate-temperature fuel cell electrolytes. Fuel cells that operate at intermediate temperatures are of importance for the DoD mission, and basic research aimed at improving the functionality of these devices is of interest to the Electrochemistry Program in the Army Research Office’s (ARO) Chemical Division. In addition, achieving the goals of our project will lead to new research.

To achieve the goals of our project we proposed four types of experiments to be carried out over a three-year period:
1) investigate the dehydration and chemical decomposition of CDP using a multi-technique approach
2) use time-resolved diffraction, and ac-impedance spectroscopy to investigate the structure, proton conductivity, and conduction mechanisms in the CDP (cubic) / $Cs_2H_2P_2O_7$ mixtures
3) use x-ray diffraction, impedance spectroscopy and neutron scattering methods to investigate the temperature-dependent structural and proton conductivity behavior of other phosphate solid acids and their mixtures
4) investigate the high-temperature microscopic structures, proton conduction mechanisms, and the thermal stability of composites based on CDP or RDP and different types of silica. We chose SiO_2 because recent studies

have shown the feasibility of synthesizing solid acid / SiO2 composites, as well as an increase in their room-temperature conductivity with respect to that of the pure solid acid

During the first two years of our project we have performed experimental work based on x-ray diffraction and impedance spectroscopy methods on CDP, CDP/SiO2, different phosphate solid acids and their mixtures (e.g. CsxRb1-xH2PO4), and other proton conductors. We have also actively involved undergraduate and graduate students and postdoctoral scholars in this type of research, and managed to leverage the funds received from this grant and secure significant additional internal funding for personnel (one more postdoc and two more graduate students), travel to conferences, as well as for the development of a new, state-of-the art proton conductivity measurement system.

During the last year of our project, we have focused on time- and temperature-resolved studies of the superprotonic CDP phase stability. In all, we published six manuscripts and submitted one more, and five of our graduate students completed their degrees: two M.S. in Physics and three in Materials Science and Engineering. Following an internship at Fort Bliss, one graduate student secured employment with Sandia National Laboratory, and one of our postdocs currently works at Los Alamos National Laboratory. Our most notable achievement is the first observation of a superprotonic CDP phase that is stable for 40 hours in air without the use of high-pressure or high humidity sample environments.

Accomplishments: Below, we summarize our achievements during the performance period of the project within the following categories:
1) Scientific/Discovery
2) Publications
3) Student/Postdoc supervision and degree completion
4) Fund Matching and Research Infrastructure Development

In addition, we uploaded a file including relevant data and a more detailed discussion of our major results (please see “UPLOAD” section).

1) Scientific/Discovery Achievements:
Clearly, our most important research achievement was the stabilization of the superprotonic CDP phase without the use of a special high-pressure or high-humidity sample environment. Our data unequivocally shows that the cubic (Pm3m) phase of CDP is stable in ambient (dry) air if the sample is sealed in a glass chamber, and that its superprotonic conduction persists at ~1.5×10-2 S·cm-1 over a timespan t=40 h at a temperature T=260oC. The experiment is reproducible, and there are no traces of any dehydration products in the sample (see “UPLOAD” section for supporting data, figures and discussion).
Another notable result was the first time synthesis of a CsH2PO4/SiO2 composite that exhibits a two order of magnitude proton conductivity increase (over pure CsH2PO4) in air for over 10 hours at T=260oC (see “UPLOAD” section for supporting data, figures and discussion).
During the first two years of the project we obtained two sets of “preliminary” results – first related to Goal 1 and second related to Goal 2 – that eventually led to the above-mentioned discoveries (see “UPLOAD” section for supporting data, figures and discussion of these two sets of results):
- A three order of magnitude jump in the proton conductivity is observed in CDP pellets pressed at 0.6 GPa upon heating to ~235°C even in the absence of a special (high pressure or high humidity) atmosphere.
- A polymorphic phase transition from monoclinic to cubic CDP is observed under the same pressure and humidity conditions. However, the transition does not occur through the entire volume of the sample and dehydration (observed through the formation of cesium pyrophosphate) follows immediately and is complete upon further heating by just a few degrees.
- We have found that the high proton conductivity reached at ~235°C persists upon further heating to 275°C. This is a notable and unexpected finding, as it clearly shows that a high proton conductivity can be achieved in these samples at temperatures above 235°C, without a special high pressure or high humidity atmosphere, and in the presence of the dehydration product cesium pyrophosphate.

and
- We have successfully synthesized CDP/SiO2 composites of various CDP fractions (from 90% to 30%) and found that although the composition does have a slight effect on the structural and chemical modifications undergone by CDP around 235°C, dehydration occurs in all cases upon further heating by less than 10°C.
- We have synthesized single-crystals of RbxCs(1-x)H2PO4 (0≤x≤1), and carried out, for the first time, a single crystal x-ray diffraction investigation of this system identifying new phases and shifts in the polymorphic structural

transition temperatures.

- We have uncovered direct evidence (from temperature-resolved impedance spectroscopy) that adding silica to CDP leads to a significant (nearly two-order of magnitude) increase in the proton conductivity of the CDP/SiO2 composites with respect to pure CDP at temperatures around 275°C. Moreover, the composites show a monotonic increase in the proton conductivity upon heating above the 235°C (as opposed to CDP), and we found a remarkable, five-order of magnitude increase in the proton conductivity of 70%CDP/30%SiO2 within the 195°C - 275°C temperature range. Clearly this is our most important result during the current reporting period and a key finding for the entire project as it unambiguously demonstrates the validity of our central hypothesis: that mixing these solid acids with dispersed oxides such as SiO2 leads to enhanced proton conductivities and possibly to stable compounds at intermediate temperatures.

2) Publications

We have published five times in ISI-indexed international journals and one more article on our most recent results are currently under review. These publications are listed below:

Journal Publications (*undergraduate student, **graduate student/postdoc coauthor):

- C. E. Botez, H. Martinez**, and J. L. Morris*, “X-ray diffraction investigations of structural modifications in In-doped tin pyrophosphates”, Mater. Chem. Phys. 196, 137 (2017).
- S. Fortier, J. R. Aguilar-Calderon, B. Vlaisavljevich, A. J. Metta-Magana, A. G. Goos**, and C. E. Botez, “An N-tethered uranium (III) arene complex and the synthesis of an unsupported U-Fe bond”, Organometallics, 36, 4591 (2017).
- E. M. Deemer**, P. K. Paul, F. S. Manciu, C. E. Botez, D. R. Hodges, Z. Landis, T. Akter, E. Castro, and R. R. Chianelli, “Consequence of oxidation method on graphene oxide produced with different size graphite precursors”, Mater. Sci. Eng. B 224, 150 (2017).
- J. H. Leal**, H. Martinez**, I. Martinez**, A. D. Price**, A.G. Goos**, and C. E. Botez, “Stability of the superprotonic conduction of (1-x)CsH2PO4 / xSiO2 (0≤x≤0.3) composites under dry and humid environments”, Mat. Today Commun. 15, 11 (2018).
- A. G. Goos, A. J. Encerrado Manriquez, H. Martinez, A. D. Price and C. E. Botez “Structural modifications in the RbxCs1-xH2PO4 (0≤x≤1) superprotonic conductor series: a single-crystal x-ray diffraction and impedance spectroscopy study”, J. Phys. Chem. Solids 118, 220 (2018).

Manuscript Under Review (*undergraduate student, **graduate student/postdoc coauthor):

- C. E. Botez, I. Martinez**, A. D. Price** I. Martinez**, and J. H. Leal**, “Superprotonic CsH2PO4 in dry air”, under review, J. Phys. Chem. Solids (2018).

3) Student/Postdoc supervision and degree completion

The following students have completed their degrees under the PI’s direct supervision during the reporting period:

- Mahesh Koirala – M.S. in Physics
- Andres Encerrado Manriquez – M.S. in Physics
- Andrea Montgomery – M.S. in Physics
- Heber Martinez – Ph.D. in Materials Science
- Israel Martinez – Ph.D. in Materials Science
- Alex Price – Ph.D. in Materials Science
- Matthew Hilding – B.S. in Physics
- Joshua Morris – B.S. in Physics
- Sonam Lhamo – B.S. in Physics
- Victor Gonzalez – B.S. in Biology

The PI has also supervised two postdocs:

- Alan Goos
- Juan Leal

Upon graduation, Andrea Montgomery was hired by Sandia National Laboratory, Dr. Juan Leal by Los Alamos National Laboratory, and Drs. Heber Martinez and Alan Goos secured employment in higher education
.

4) Fund Matching and Research Infrastructure Development

We secured matching funds, both from the College of Science and from the Dr. C. Sharp Cook Endowment. We have completed the installation of the impedance spectroscopy system based on a Probostat® sample holder and we also purchased and commissioned a new TGA/DSC apparatus. In all, the matching funds for this project during the past two years exceed $150,000, which allowed us to equip our laboratory with ion conductivity and thermal transport instrumentation in addition to the existing x-ray scattering capabilities.

Training Opportunities: Nothing to report

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Results Dissemination:
We have disseminated our results at the following conferences:

- Fall 2015 Joint Meeting of the Texas Section of the AAPT, Texas Section of the APS and Zone 13 of the Society of Physics Students, October 29–31, 2015

Doped Pyrophosphates as Fuel Cell Electrolytes
Heber Martinez, Joshua Morris, Cristian Botez

- Southwest Emerging Technology Symposium 2016, Wyndham El Paso Airport in El Paso, Texas, April 9th, 2016

Conductivity of Cs1-xSixH2PO4 trough Impedance spectroscopy: temperature dependence study
Andrea Montgomery, Andres J. Encerrado M., Israel Martinez, Ben Deutsch, Victor Gonzalez, Alan Goos and Cristian Botez

Synthesis and Characterization of Cs1-xRbxH2PO4 and SiO2 Mixtures.
Benjamin Deutsch, Victor Gonzalez, Juan H. Leal, Alex Price, and Cristian Botez

Single Crystal Structures of Cs1-xRbxH2PO4: Site occupancy, phase, and structural changes
Alan Goos, Alex Price, and Cristian Botez

- 66th Annual Meeting American Crystallographic Association (ACA) Denver CO, July 22-26, 2016

Synthesis and Characterization of Cs1-xH2PO4 and SiO2 Mixtures as Electrolytes
Benjamin Deutsch, Victor Gonzalez, Juan Leal, Alex Price, and Cristian Botez

Conductivity of Cs1-x SixH2PO4 through Impedance Spectroscopy:Temperature Dependence Stydy
Andres J. Encerrado M., Andrea Montgomery, Israel Martinez, Ben Deutsch, Victor Gonzalez, Alan Goos and Cristian Botez

Proton conduction and chemical stability of the high-temperature cubic CsH2PO4 modification
Israel Martinez, Andres J. Encerrado M., Victor Gonzalez, Alan Goos and Cristian Botez

- Green Chemistry, Gordon Research Conference, Commercial Successes and Remaining Challenges After a Twenty Year Investment in Green Chemistry Principles, July 31- August 5, 2016, Stoweflake Conference Center Stowe, VT

Structure and Conductivity of Solid Acid Materials: impedance spectroscopy and X-ray diffraction
Alan Goos, Andres J. Encerrado M., Alex Price, Israel Martinez, Victor Gonzalez, Juan Leal, and Cristian Botez

- Joint Meeting of the Four Corners and Texas Sections of the American Physical Society Volume 61, Number 15 Friday-Saturday, October 21-22, 2016; Las Cruces, New Mexico

Crystalline Structure of Solid Acid Under different partial pressures
Alexandra Dominguez, Cristian Botez

Conductivity of Cs1-xSixH2PO4 through Impedance spectroscopy: Partial pressure and temperature dependence study
Mathew Hilding, Cristian Botez

EPR Study of Superparamagnetismin Mn3O4 Nanoparticle Ensembles
Mahesh Koirala, Alex Price, Ronald Tackett and Cristian Botez

Indium Doping Induced Lattice Constant Variation in Tin Pyrophosphate
Heber Martínez, Josh Morris, Cristian Botez

- University of Texas at El Paso Graduate Student Research Expo, Friday, November 11, 2016, Hilton Garden

Inn (HGI), El Paso Texas

Cesium Dihydrogen Phosphate (CsH_2PO_4) Stability at superprotonic behavior temperatures.
Israel Martínez, Alex Price, Cristian Botez

Doped Pyrophosphates as Fuel Cell Electrolytes
Heber Martínez, Josh Morris, Cristian Botez

- Joint Spring 2017 Meeting of the Texas Sections of APS, Texas Section of AAPT, and Zone 13 of the Society of Physics Students, March 9-11, 2017, San Antonio College, San Antonio, TX

The effect of time on the dehydration of CsH_2PO_4 at 260°C using XRD
Andrea Montgomery, Israel Martinez, Juan Leal, Alan Goos, Alex Price, Heber Martinez and Cristian Botez

- First CONACyT Grant Holders Meeting in North America, March 14-16, 2018, Washington, DC

Chemical Stabilization of CsH_2PO_4 proton conductivity by the usage of hermetically sealed chamber at intermediate temperatures)
Israel Martinez

Honors and Awards: During the performance period of the project, the PI has received the following Honors and Awards:

- The Dr. C. Sharp Cook Chair in Physics endowment. This is the most prestigious endowment in the Department of Physics, and one of the only two Endowed Chair positions in the College of Science. Funds from this endowment helped us operate our research laboratory, improve our research infrastructure, and enhance the participation of our students in research conferences.
- University Award for Outstanding Efforts in Securing Extramural Funding from the Office of Research and Sponsored Projects. This is a University wide award that, in the PI's case, is related to securing this and previous funding for major instrumentation from the Department of Defense.
- College of Science Undergraduate Student Choice Award for Outstanding Teaching, an award based on student votes and related to in-class teaching and student research and career mentoring. The award and related activities significantly helped us with undergraduate student recruitment for research in our laboratory.
- Nominated to run for the Chair line of the Texas Section of the American Physical Society.

Protocol Activity Status:

Technology Transfer: We have met with LTC John Mark Thane, the Executive Officer of the Capability Package Directorate, Army Rapid Capabilities Office at Fort Bliss. During Colonel Thane's visit we discussed several aspects of the progress made by our group and our Department following receiving DoD funding, including research/discovery, capability building and student opportunities. Colonel Thane expressed interest in expanding the internship opportunities for UTEP Physics students as well as in possible further collaborations and joint projects with our Department.

- Upon graduation, Andrea Montgomery, one of our M.S. students, secured employment as Operations Research Analyst in the Materiel Test Directorate at Sandia National Laboratory

In addition, we continued our interactions with members of the MPA 11 Group at Los Alamos National Laboratory (LANL) and we plan to submit a proposal to fund a joint program where our faculty and students will be engaged in multidisciplinary research projects that are initiated and carried out primarily at UTEP but have a well-defined component to be performed at LANL.

- Juan Leal, one of our postdocs who worked on the project, was employed by the MPA 11 Group at Los Alamos National Laboratory.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Cristian Botez
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:

International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Juan Leal
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Alan Goos
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Alex Price
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Heber Martinez
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Israel Martinez
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Andrea Montgomery
Person Months Worked: 6.00 **Funding Support:**

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Andres Encerado
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Sonam Lhamo
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Participant: Alexandra Dominguez
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Mathew Hilding
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Joshua Morris
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Joshua Morris

Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Taylor Hernandez
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Benjamin Deutsch
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Technician
Participant: Victor Gonzalez
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: High School Student
Participant: Pierce Davis
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

DISSERTATIONS:

Publication Type: Thesis or Dissertation
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Date Received: 31-Aug-2017 Completion Date: 5/20/17 12:00PM
Title: STRUCTURAL MODIFICATIONS IN THE RbxCs1-xPO4 (0 ? x ? 1) SUPERPROTONIC CONDUCTOR SERIES: A SINGLE-CRYSTAL X-RAY DIFFRACTION AND IMPEDANCE SPECTROSCOPY STUDY.
Authors: ANDRES JOSE ENCERRADO MANRIQUEZ
Acknowledged Federal Support: **Y**

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Institution: University of Texas at El Paso
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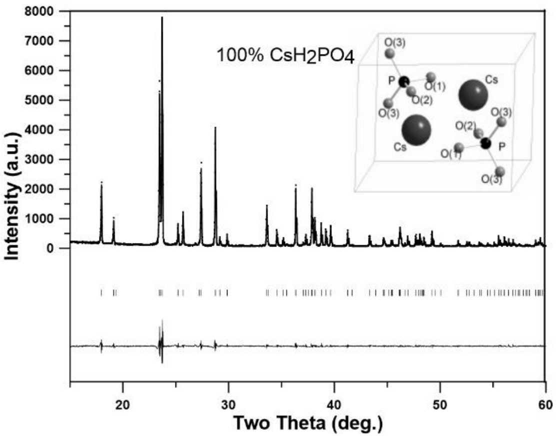
Authors: HEBER JAIR MARTINEZ SALINAS
Acknowledged Federal Support: **Y**

Scientific progress (2015-2018)

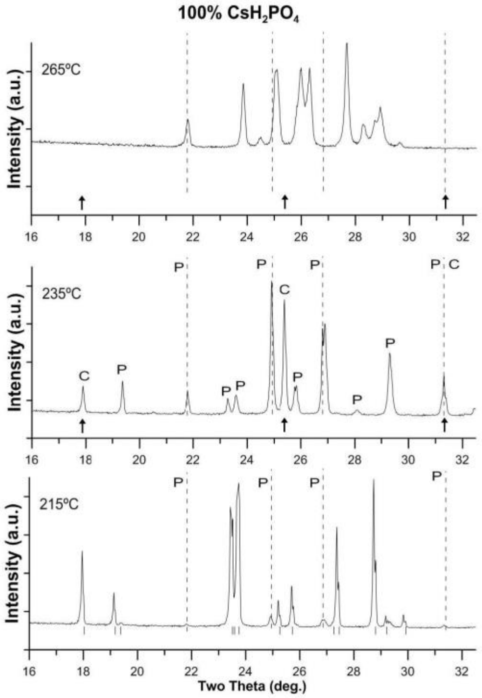
1) Our first findings related to the first goal of the project: *to determine the microscopic and macroscopic (proton conductivity) modifications that accompany the dehydration and chemical decomposition of phosphate solid acids*, are the following:

We have synthesized CsH_2PO_4 (CDP) powders and checked their quality through powder x-ray diffraction as shown in Figure 1 (a). We then carried out temperature-resolved x-ray measurements within the 215^oC - 265^oC temperature range (Figure 1 (b)), and found that under ambient pressure and humidity conditions both the CDP polymorphic transition (monoclinic-to-cubic) and its dehydration are observed. Eventually, the sample dehydrates completely.



<u>Figure 1 (a)</u> X-ray diffraction pattern (solid symbols) and full profile, Le Bail fit (solid line) confirming the RT crystal structure of CDP and the lack of impurities in the sample. The inset shows the unit cell of the RT CDP monoclinic structure.

We then used impedance spectroscopy to measure and analyze the proton conductivity behavior of CDP pellets pressed at 0.6GPa from powders previously analyzed by x-ray diffraction. Figures 2(a) and 2(b) show our impedance spectroscopy data collected upon heating within two temperature ranges: 200^oC to 220^oC, and 240^oC to 250^oC, respectively. There is a clear difference between the shape of the Nyquist plots measured above and below 230^oC. In the lower temperature range, and for frequencies between 1MHz and 1kHz, we observed the typical semicircles and large values for the real and imaginary parts of the impedance, as expected for this system.



<u>*Figure 1 (b)*</u> Temperature-resolved x-ray data collected in air upon heating 100%CDP powders from 215°C to 265°C. It shows the polymorphic transition from monoclinic to cubic CDP as well as its chemical decomposition via dehydration. The vertical markers in the lower panel correspond to the monoclinic $P2_1/m$ CDP phase, the peaks marked by (P) to the initial dehydration product $Cs_2H_2P_2O_7$, and the ones marked by vertical arrows to the cubic (C) Pm-3m phase of CDP. At 265°C (upper panel) the entire pattern corresponds to the final dehydration product

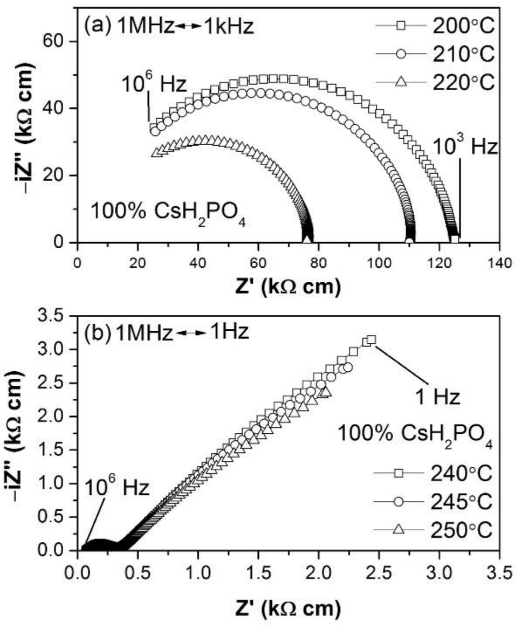


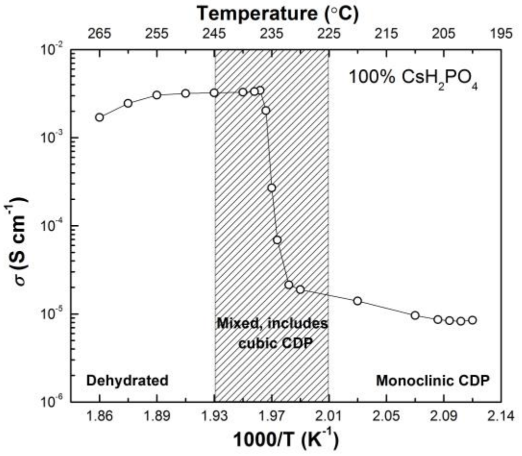
Figure 2 Nyquist plots collected on pure CDP within two temperature ranges (a) 200ºC to 220ºC and (b) 240ºC to 250ºC

The resulting proton conductivity is low, of the order of 10^{-5} S cm^{-1}. In the higher temperature range (above 240ºC), the Nyquist plots are markedly different, the real and imaginary impedances have much lower values, and an almost linear behavior is observed to persist down to 1Hz (as shown in Figure 2(b)). Most importantly, the resulting proton conductivity reaches almost 10^{-2} S cm^{-1}, nearly three orders of magnitude higher than in the lower temperature range.

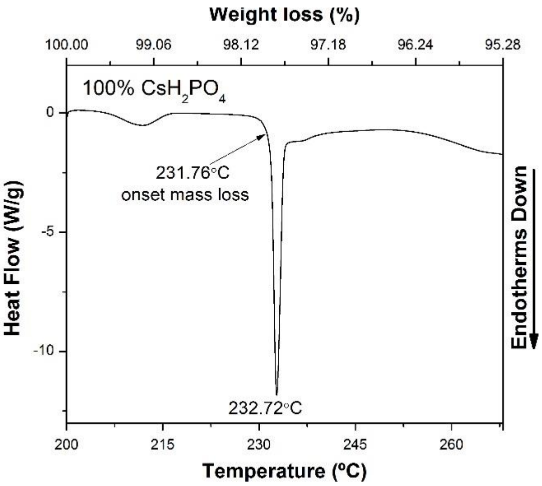
Now, it is important to corroborate these temperature-resolved proton conductivity results with their structural, x-ray diffraction counterparts. As our x-ray data and analysis indicates, monoclinic CDP is the dominant phase within the lower temperature range). The structural data also shows that the monoclinic-to-cubic polymorphic transition initiates right below 220ºC (probably from the surface of the grains), a robust cubic phase is present at 235ºC together with the initial dehydration product $Cs_2H_2P_2O_7$. Eventually the entire cubic CDP phase dehydrates at 265ºC.

The first two findings from these combined x-ray diffraction – impedance spectroscopy experiments are not unexpected. Indeed, the monoclinic (RT phase) of CDP is known to have a relatively low proton conductivity, and a several-order-of-magnitude jump in the proton conductivity upon heating has been observed before in CDP upon heating to ~235ºC, but under a saturated water vapor atmosphere. The sudden proton conductivity increase is believed by most to be due to the polymorphic phase transition from monoclinic to cubic CDP, and the chemical instability of cubic CDP (in the absence of special conditions: high humidity or high pressure) is regarded as the main barrier to progress towards the large scale use of use of CDP and other phosphate-based solid acids as fuel cell electrolytes. As indicated above, our x-ray data show the presence of a robust cubic phase at ~235ºC (even in the absence of a high humidity/pressure atmosphere), and this could explain the three-order-of-magnitude proton conductivity jump observed in our impedance spectroscopy measurements. Remarkably, however, the high proton conductivity apparently triggered by the cubic CDP phase formation seems to persist within a temperature range where, according to our x-ray measurements, CDP dehydrates and its cubic phase is not present any longer. This is illustrated in Figure 3 (a), which shows the temperature dependence of the proton conductivity of 100% CDP determined from impedance spectroscopy measurements (as the ones in Figure 2) carried out on pellets pressed at 0.6 GPa. The temperature regions discussed above are clearly indicated, including the one above 245ºC where x-ray results show that CDP powders completely dehydrate.

While we believe this is, indeed, a notable finding, a number of aspects need to be clarified. First, the x-ray data were collected on powders and the impedance spectroscopy measurements were carried out on pressed pellets. Moreover, the two experimental settings were different, and although we do not anticipate significant issues with the temperature measurement and stability, we need to indicate that for the impedance spectroscopy measurements the thermocouple was attached to the pellet, whereas for the x-ray experiment the thermocouple was about 0.5 mm away from the sample holder containing the powder. Finally, to make sure that the sample has indeed undergone dehydration in the higher temperature range in Figure 3 (a), we carried out differential scanning calorimetry (DSC) experiments on CDP pellets. The results are shown in Figure 3 (b) and reveal a thermal event that can be associated to dehydration at ~233°C, i.e. exactly at the temperature where the proton conductivity jump initiates.



<u>Figure 3 (a)</u> Temperature dependence of the proton conductivity of pellets pressed at 0.6 GPa from pure CDP powders. Cubic CDP is present in the powders within the hatched temperature range.



<u>*Figure 3 (b)*</u> Differential scanning calorimetry (DSC) *measurements carried out on CDP pellets indicate that weight loss initiates at ~232°C and confirms the dehydration of the CDP cubic phase.*

2) Our results related to the second goal of the project: to *synthesize composite materials based on phosphate solid acids and highly dispersed oxides, and to investigate the crystal structures, proton conduction, and thermal stability of their high temperature phases*, are the following:

We have successfully synthesized (1-x)CsH_2PO_4 / xSiO_2 composites by mechanically mixing CDP with silica nanopowders (10-20 nm particle size) for approximately 30 minutes. Composites of x values (on a mole basis) 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 were produced and characterized by Energy Dispersive X-Ray Spectroscopy (EDS) measurements of the Cs:Si mole ratio. We then pressed pellets of CDP/SiO_2 composites at 0.6 GPa and carried out similar measurements as the ones done on pure CDP. Our main finding here came from temperature-resolved impedance spectroscopy measurements. As shown in Figure 4, we observe that mixing CDP with nano-silica leads to a major two-order of magnitude increase in the proton conductivity at temperatures above 260°C. Furthermore, as opposed to pure CDP (triangles) where the proton conductivity, σ, exhibits a slight decrease upon heating from 235°C to 275°C, σ increases with increasing T for CDP/SiO_2 composites (circles and squares). Finally, we find that the proton conductivity of the 70%CDP/30%SiO_2, x=0.3 sample (circles), increases by four orders of magnitude within the 195°C - 275°C temperature range reaching ~10 S cm^{-1}.

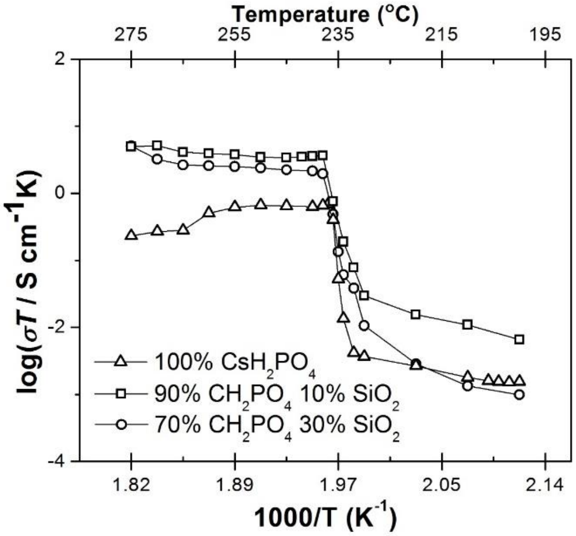


Figure 4 Temperature dependence of the proton conductivity of pellets pressed at 0.6 GPa from pure CDP (triangles), 90%CDP/10%SiO_2 (squares), and 70%CDP/30%SiO_2 (circles) powders.

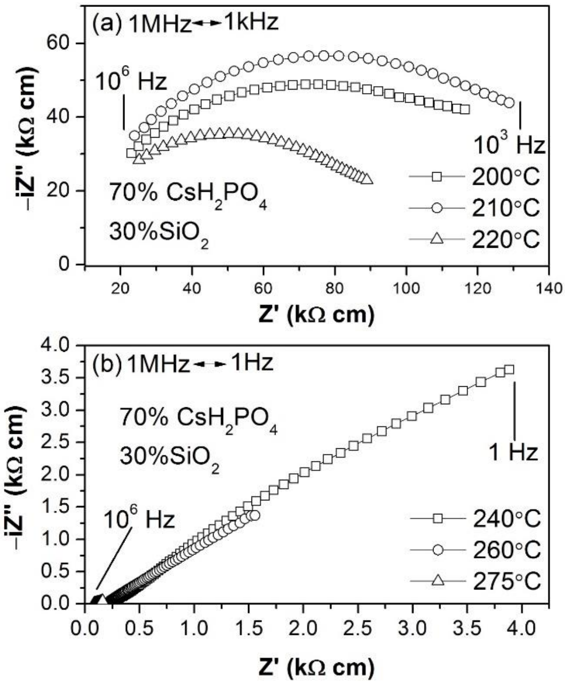


Figure 5 Nyquist plots collected on pure CDP within two temperature ranges (a) 200°C to 220°C and (b) 240°C to 275°C

Clearly, this is an important finding as it confirms our hypothesis that mixing CDP with SiO_2 nano-powders improves the thermal stability of the composite (compared to pure CDP) *and* increases the overall proton conductivity at intermediate temperatures. Further confirmation comes from the data presented in Figure 5. At lower temperatures, between 200°C to 220°C, the data collected on the 70%CDP/30%SiO_2 (x=0.3) sample (Figure 5 (a)) exhibits a very similar behavior to the one of its pure CDP counterpart (Figure 2(a)). On the other hand, the Nyquist plots collected at higher temperatures (above the monoclinic→cubic CDP transition and within the range where the CDP dehydration occurs) show a clear difference between pure CDP (Figure 2(b)) and the 70%CDP/30%SiO_2 (x=0.3) composite (Figure 5(b)). Indeed, the small semicircles at high frequencies (an indication of a lower-quality proton conduction) are present for pure CDP, but *completely* disappear upon mixing CDP with 30% nano-silica, where the Nyquist plots show a nearly linear behavior over a broad range of frequencies, a signature of a highly efficient proton conduction.

Finally, we have successfully used single-crystal x-ray diffraction to investigate the structural modifications induced by Rb-doping of CsH_2PO_4. We found that the monoclinic $P2_1/m$ CsH_2PO_4 modification persists within the $Rb_xCs_{1-x}H_2PO_4$ ($0 \le \mathbf{x} \le 1$) series upon Rb-doping from x=0.1 to x = 0.7. $Rb_{0.8}Cs_{0.2}H_2PO_4$ (x=0.8), however, exhibits a previously unreported $P2_1/c$ monoclinic phase, 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_2PO_4.

Table I shows the crystal structures of the mixed solid acids $Rb_xCs_{1-x}H_2PO_4$ determined from SC-XRD experiments for x= 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9. One notes that the well-known crystal structure of the undoped compound (x=0) – monoclinic $P2_1/m$ – persists upon increasing the Rb content up to x=0.7 ($Rb_{0.7}Cs_{0.3}H_2PO_4$). Further doping to x=0.8, however, results in several structural changes. Indeed, for $Rb_{0.8}Cs_{0.2}H_2PO_4$ the mirror plane is lost, the unit cell doubles in size along the **a** axis, and the space group changes over to $P2_1/c$. 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, this time from monoclinic to tetragonal (I-42d).

Cation ratio	$Rb_{0.9}Cs_{0.1}$	$Rb_{0.8}Cs_{0.2}$	$Rb_{0.7}Cs_{0.3}$	$Rb_{0.6}Cs_{0.4}$	$Rb_{0.5}Cs_{0.5}$	$Rb_{0.4}Cs_{0.6}$	$Rb_{0.3}Cs_{0.7}$	$Rb_{0.2}Cs_{0.8}$	$Rb_{0.1}Cs_{0.9}$
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	I -42d	P 2(1)/c	P 2(1)/m	P 2(1)/m	P 2(1)/m	P 2(1)/m	P 2(1)/m	P 2(1)/m	P 2(1)/m
T (ºC)	25	25	25	25	25	25	25	25	25
Unit cell dimensions (Å, °)									
a	7.6067(3)	9.5663(5)	4.7932(4)	4.8262(3)	4.8283(3)	4.8415(3)	4.8504(3)	4.8610(3)	4.8728(2)
b	7.6067(3)	6.2161(4)	6.2319(5)	6.2771(3)	6.2908(4)	6.3074(3)	6.3283(3)	6.3538(3)	6.3776(3)
c	7.2942(3)	7.7067(4)	7.6689(6)	7.7627(5)	7.7772(5)	7.8076(5)	7.8276(4)	7.8611(4)	7.8894(4)
α	90	90	90	90	90	90	90	90	90
β	90	108.852(2)	107.606(3)	107.921(3)	108.024(2)	108.01(1)	107.879(2)	107.739(2)	107.739(2)
γ	90	90	90	90	90	90	90	90	90
Volume ($Å^3$)	422.06(4)	433.70(4)	218.35(3)	223.76(2)	224.63(2)	226.74(2)	228.66(2)	231.25(2)	233.52(2)
Z	4	4	2	2	2	2	2	2	2
Calculated density (g/cm^3)	4.963	4.830	4.797	4.681	4.893	4.619	4.580	4.529	4.485
Absorption coefficient (mm^{-1})	20.491	19.941	19.805	19.326	11.718	19.071	18.911	18.699	18.518
2θ range	7.576 to 56.41°	5.586 to 62.01°	5.58 to 56.64 °	8.521 to 54.37°	6.48 to 61.30°	5.49 to 61.05°	8.44 to 61.12°	6.41 to 56.63°	5.42 to 56.58°
Unique reflections	265	1452	598	539	747	745	757	631	635
Total reflections	3632	10419	10836	5586	11284	8448	4927	8604	7654
Goodness-of-fit on F^2	1.316	1.080	1.126	1.169	1.253	1.178	1.163	1.189	1.428
R_1, wR_2 (all data)	R1 = 0.0334 wR2 = 0.0841	R1 = 0.0517 wR2 = 0.0677	R1 = 0.0381 wR2 = 0.0905	R1 = 0.0512, wR2 = 0.1110	R1 = 0.0248 wR2 = 0.0687	R1 = 0.0232 wR2 = 0.0572	R1 = 0.0336 wR2 = 0.0602	R1 = 0.0167 wR2 = 0.0419	R1 = 0.0255 wR2 = 0.0629
R_1, wR_2 (final)	R1 = 0.0327 wR2 = 0.0835	R1 = 0.0320 wR2 = 0.0622	R1 = 0.0364 wR2 = 0.0895	R1 = 0.0403, wR2 = 0.1053	R1 = 0.0237 wR2 = 0.0681	R1 = 0.0221 wR2 = 0.0566	R1 = 0.0262 wR2 = 0.0578	R1 = 0.0159 wR2 = 0.0415	R1 = 0.0244 wR2 = 0.0625
F(0 0 0)	564	564	282	282	296	282	282	282	282

*Table I: Crystallographic data on the $Rb_xCs_{1-x}H_2PO_4$ (0 ≤ **x** ≤ 1) series obtained from single crystal data analysis*

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 is shown in Figure 6. Here, we first note that the length of all three unit-cell axes decreases monotonically with increasing x within the monoclinic $P2_1/m$ (0 ≤ **x** ≤ 0.7) range, an expected behavior as smaller Rb atoms (ionic radius 161 pm) progressively replace their larger Cs counterparts (ionic radius 174 pm).[30] The unit cell volume V decreases linearly with the amount of rubidium, in accordance with Vegard's law. The monoclinic symmetry persists at x=0.8, but the space group changes from $P2_1/m$ to $P2_1/c$ 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 continue their decrease. The unit-cell volume of the x=0.8 compound reaches ~434 Å^3 (compared to its x=0.7 counterpart ~218 Å^3) and the number of formula units in the unit cell doubles from 2 to 4. This is the first observation of a $P2_1/c$ structure within the $Rb_xCs_{1-x}H_2PO_4$ series.

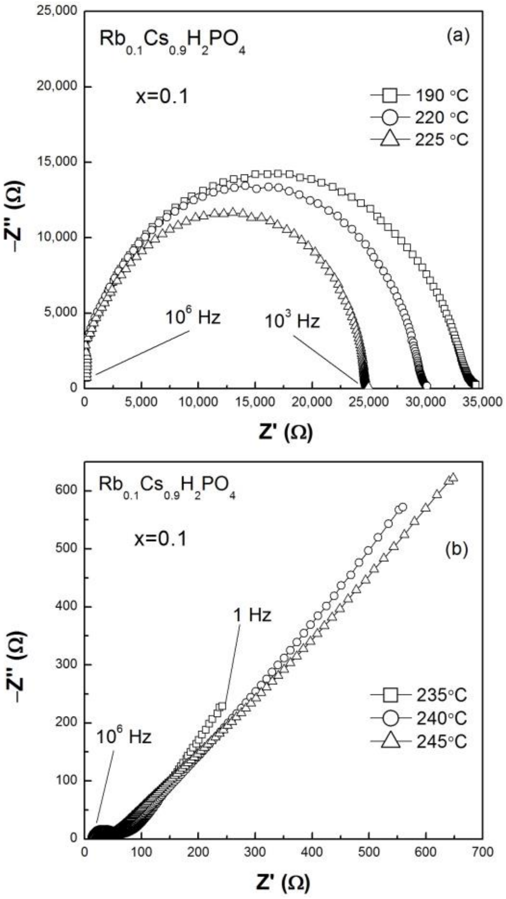


*Figure 7 Nyquist plots (out-of-phase Z'' vs. in-phase Z' impedance) collected on $Rb_{0.1}Cs_{0.9}H_2PO_4$ (**x** =0.1) at (a) T=200°C (squares), T=220°C*

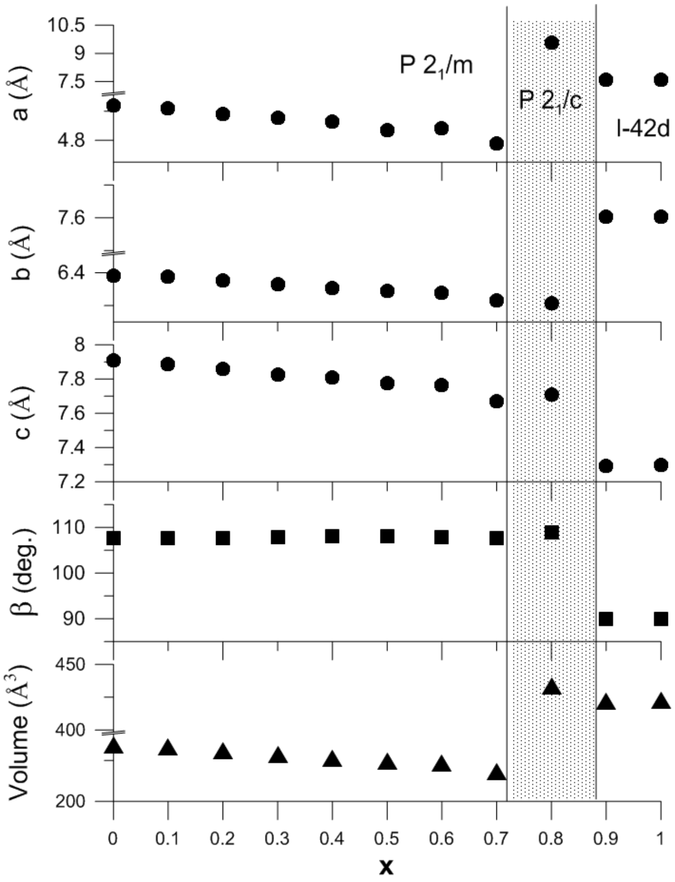


Figure 6 Unit cell parameters and volume as a function of the Rb-doping level x in the three crystallographic phases present in the $Rb_xCs_{1-x}H_2PO_4$ ($0 \leq \mathbf{x} \leq 1$) series

Next, we carried out impedance spectroscopy measurements on low and high Rb-doping level members of the $Rb_xCs_{1-x}H_2PO_4$ 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.

Figure 7, shows Nyquist plots: out-of-phase (Z") vs. in-phase (Z') impedance measured on $Rb_{0.1}Cs_{0.9}H_2PO_4$ (x=0.1) at different temperatures within the 190°C – 245°C range. The data demonstrates the well-known transition from (a) the low proton conductivity regime (T<235°C) to (b) the supeprotonic behavior (T>235°C), which, structurally, corresponds to a monoclinic ($P2_1/m$) to cubic (Pm-3m) polymorphic phase transition. Expectedly, similar datasets were observed for all the other members of the $Rb_xCs_{1-x}H_2PO_4$ series up to x=0.7.

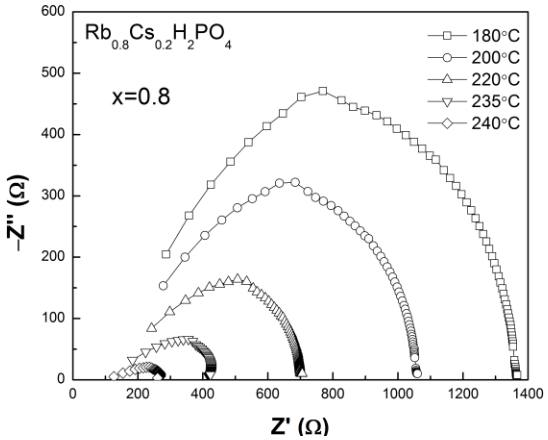


Figure 8 *Unit cell parameters and volume as a function of the Rb-doping level x in the three crystallographic phases present in the* $Rb_xCs_{1-x}H_2PO_4$ *(*$0 \leq \mathbf{x} \leq 1$*) series*

The Nyquist plots measured on $Rb_{0.8}Cs_{0.2}H_2PO_4$ (x=0.8) exhibit a markedly different behavior, as shown in Figure 8. Indeed, datasets collected at temperatures between 180^{o}C and 240^{o}C have the same shape throughout the entire temperature range, with no major changes observed upon heating above 230^{o}C (as was the case for x≤0.7) This indicates that no abrupt jump in the proton conductivity (superprotonic behavior) is observed in $Rb_{0.8}Cs_{0.2}H_2PO_4$. We also note that the shape of the Nyquist plots collected on $Rb_{0.8}Cs_{0.2}H_2PO_4$ (x=0.8) are slightly distorted (vertically elongated) from the ones recorded on the lightly Rb-doped $Rb_{0.1}Cs_{0.9}H_2PO_4$ (x=0.1), which, below the transition, are perfect semicircles. It is known that the latter correspond to the simple ion diffusion throughout the electrolyte, and can be modeled by an equivalent circuit that includes a resistor R and a constant phase element Q of impedance $Z_Q(\omega) = [Y(i\omega)^n]^{-1}$ placed in parallel (where ω is the frequency, and Y and n are constants). Deviations from the perfect semicircle shape in Nyquist plots are not uncommon, and usually indicate the presence of a more complex conduction process or even multiple conduction paths or mechanisms. Therefore, the shape of the impedance spectroscopy data in Figure 8 indicates that the proton conduction of the (x=0.8) sample is qualitatively different and more complex than that of the other members of the $Rb_xCs_{1-x}H_2PO_4$ ($0 \leq \mathbf{x} \leq 1$) series likely due to the broken symmetry (lost mirror plane) and the disordered nature of the newly uncovered $P2_1/c$ phase in the x=0.8 compound.

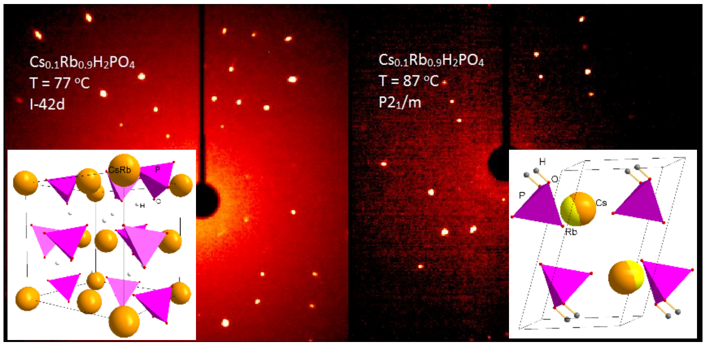


Figure 9 *Single-crystal diffraction patterns show a structural phase transition from tetragonal I-42d to monoclinic* $P2_1/m$*. The insets show unit cells of the two crystal structures.*

We also found that $Rb_{0.9}Cs_{0.1}H_2PO_4$ 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 °C) than its RbH_2PO_4 counterpart (~120 °C). Figure 9 shows single-crystal diffraction patterns collected at two different temperatures, 77 and 87°C, on a $Rb_{0.9}Cs_{0.1}H_2PO_4$ sample. Data analysis reveals a polymorphic phase transition from tetragonal I-42d to an intermediate temperature phase: monoclinic $P2_1/m$. The two structures are schematically shown in the insets. While this transition has been previously observed in observed in pure RDP, *it occurred at a temperature ~30°C higher*, which demonstrates the possibility to control the polymorphic transition temperatures of the investigated systems by using mixed phosphates.

3) Our **most significant finding** is related to the ultimate goal of the project: *to inhibit the dehydration of the superprotonic phases of phosphate solid acids in order to enable their use as electrolytes in intermediate-temperature fuel cells.*

We report the first observation of a stable superprotonic CsH_2PO_4 (CDP) phase in the absence of high humidity and high pressure. Using temperature- and time-resolved impedance spectroscopy we show that the superprotonic conductivity of a CDP pellet measured in dry air (22%rh) in a hermetically sealed chamber holds at $\sigma \sim 1.5 \times 10^{-2}$ S·cm^{-1} over a timespan t=40 h at a temperature T=260°C. Nyquist plots confirm the superprotonic nature of the conduction and x-ray diffraction data reveal that no dehydration of the CDP superprotonic phase occurs under the above-mentioned conditions.

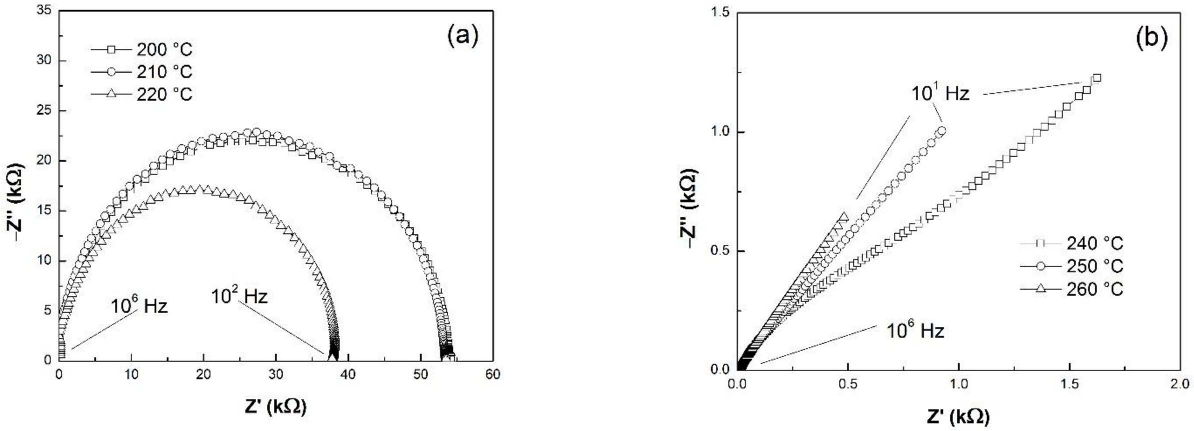


Figure 10 (a) Nyquist plots recorded at T=200°C (squares), T=210°C (circles), and T=220°C (triangles) on a CDP pellet contained in dry air (22%rh) (b) Nyquist plots recorded at T=240°C (squares), T=250°C (circles), and T=260°C (triangles) on the same CDP sample

All impedance spectroscopy measurements were carried out using a Solartron 1260 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. Silver paste was deposited on both faces of the pellet to serve as electrodes, and Pt wires were used as measurement leads. The pellet was contained in a hermetically sealed chamber filled with ~ 15 cm^3 of dry air (22%rh). The Nyquist plots collected upon heating a CDP pellet sealed in dry air from 200°C to 260°C are shown in Figure 10. As expected, the shape changes dramatically as the temperature is brought above the superprotonic transition point T_s~233°C. The most important feature of these data is the absence of any small semicircle at high frequencies for $T>T_s$ (Figure 10(b)). This already indicates the quality of the superprotonic conduction and suggests that the cubic (superprotonic) phase is the only one present in the CDP sample when sealed in dry air. It is important to mention, however, that

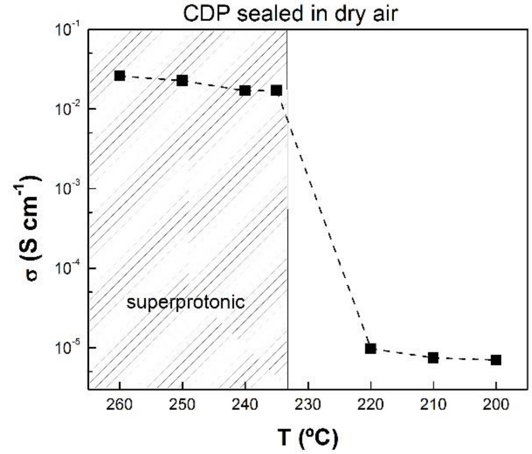


Figure 11 Temperature dependence of the proton conductivity of CDP, σ vs. T, determined from the Nyquist plots shown in Figure 1

these are temperature-resolved data that, indeed, reveal a superprotonic transition and the fact that the proton conductivity stays at very high values ($\sigma \sim 1.5\times10^{-2}$ $S\cdot cm^{-1}$) within the superprotonic temperature range (as shown in Figure 11); yet *time*-resolved impedance spectroscopy measurements at $T>T_s$ are needed to assess the stability of the superprotonic phase. These are shown in Figure 12, and so far represent the most important result we obtained in this project. The five data sets collected on a CDP sample when sealed in dry air at 260°C, 20h, 30h, 40h and 50h after reaching this temperature nearly overlap, showing essentially no change in the proton conductivity. Moreover, the straight segments that extend over four orders of magnitude of frequency demonstrate a near perfect superprotonic behavior and, as the inset shows, they all intersect the real impedance axis at 7Ω indicating that the proton conductivity does not change. We have carried out similar experiments and measured the proton conductivity of a CDP sample in dry air every hour for 40h at 260°C. The results, shown by the circles in Figure 4, demonstrate that the superprotonic conductivity stays constant at 1.5×10^{-2} $S\cdot cm^{-1}$ for 40h. This is a remarkable result, so to eliminate the possibility of an artifact we simply opened the sealed chamber and repeated the experiment. As shown by the triangles in Figure 13, the proton conductivity drops dramatically as expected for a CDP sample exposed to an open atmosphere at this temperature.

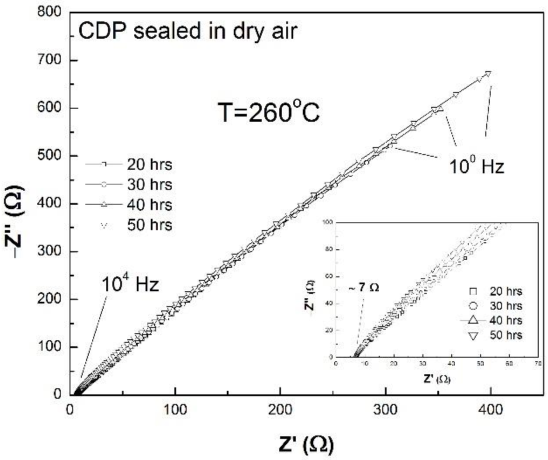


Figure 12 Time-resolved impedance spectroscopy data collected on CDP sealed in dry air and kept at T=260°C for 20 h (squares), 30 h (circles), 40 h (upright triangles), and 50 h (inverted triangles).

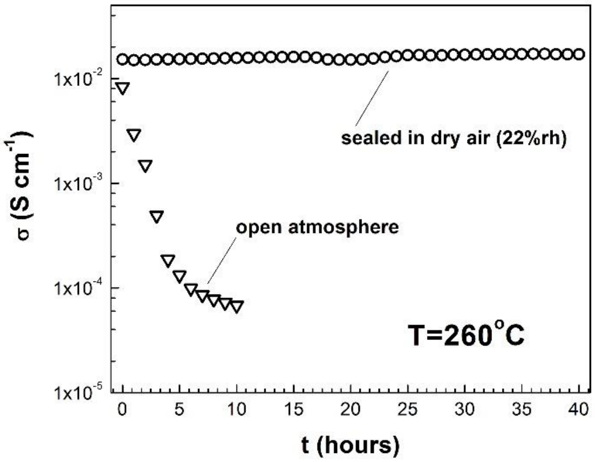


Figure 13 Time dependence of the proton conductivity measured on a CDP pellet sealed in dry air (circles) and in an open atmosphere (triangles).

In addition, to confirm that the *entire* CDP sample is indeed in the Pm3m cubic superprotonic phase when kept at 260°C in sealed dry air (22%rh) for 40h, we carried out x-ray diffraction measurements on the CDP powder used to press the pellet and on the powder obtained by grinding the pellet after being kept under the above mentioned conditions. Powder x-ray diffraction (XRD) measurements were carried out at room temperature in the reflectivity geometry on a Panalytical Empyrean diffractometer using Cu Kα radiation (λ=1.54Å). XRD patterns were recorded within the 15-60° 2θ angular range using a 0.005° step and counting 1s at each step using a position sensitive detector. Raw datasets were eventually reduced and analyzed via Rietveld refinements using the HighScore® software. It is known that the room temperature monoclinic $P2_1/m$ CDP phase undergoes a polymorphic transition to its superprotonic cubic

Pm3m counterpart at T_s and, if dehydration occurs, it is the cubic phase that changes chemically according to the reaction: $2CsH_2PO_4 \rightarrow Cs_2H_2P_2O_7 + H_2O$.

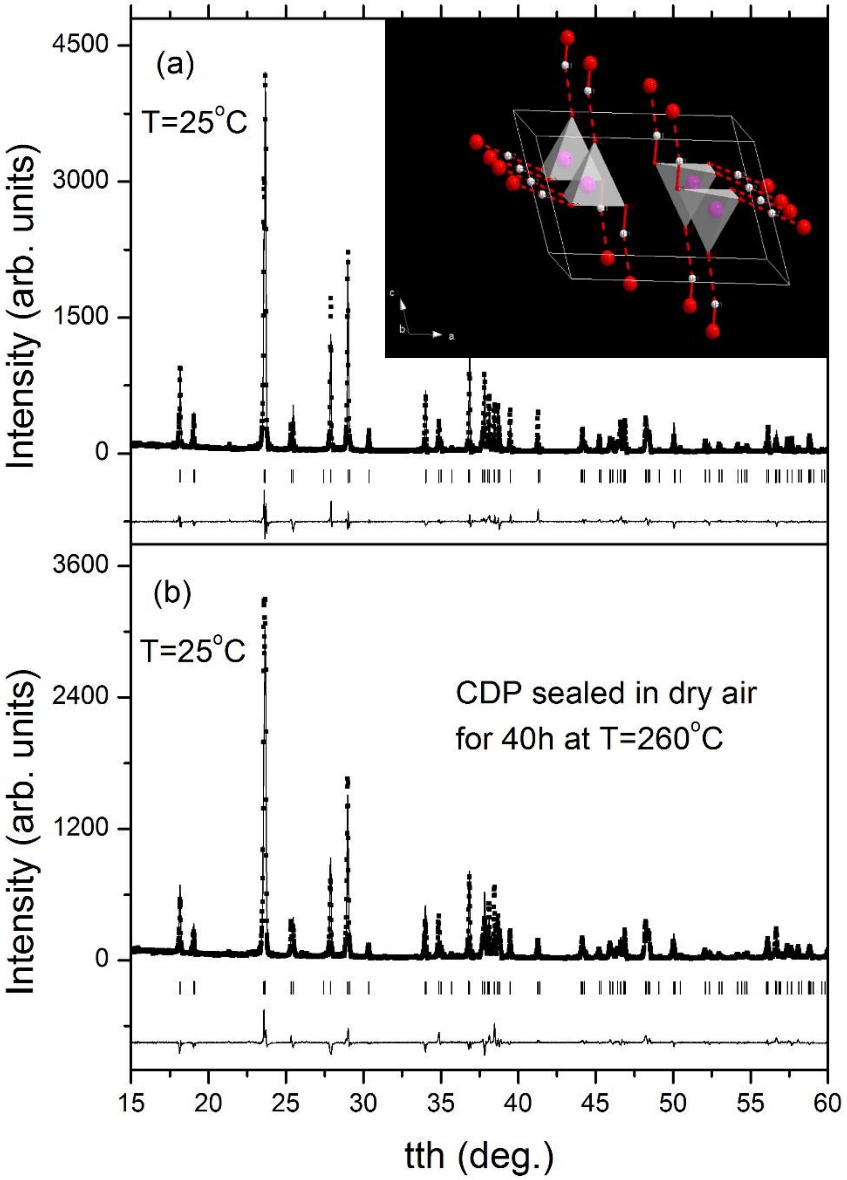
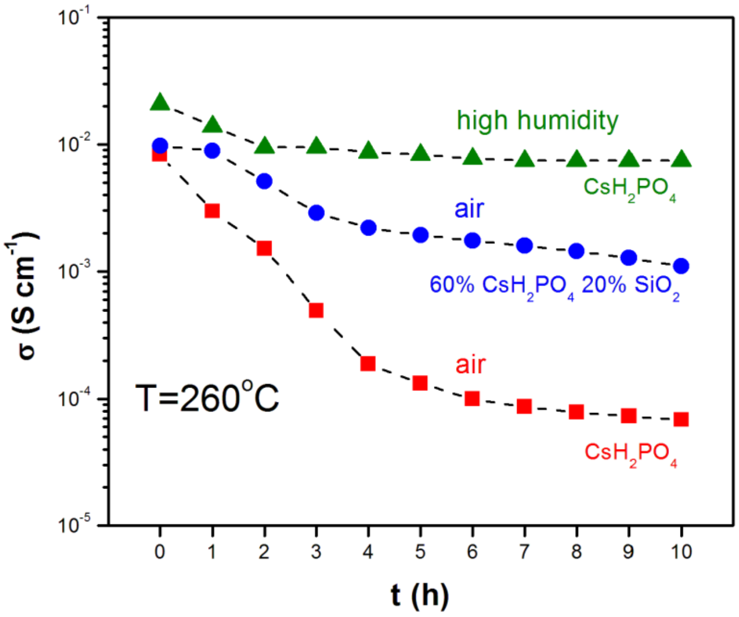


Figure 14 Rietveld refinements carried out against data collected on (a) the CDP powder used to press the pellet used in the impedance time-resolved impedance spectroscopy studies and (b) the powder obtained by grinding the pellet after being kept at 260°C in sealed dry air (22%rh) for 40h. The solid symbols are the observed intensities I_{obs} measured at detector angles (2θ) between 15 and 60 deg. The solid line represents the calculated intensities I_{calc} and the vertical bars mark the angular positions of the Bragg reflections. The lower trace is the difference curve between the observed and calculated intensities Iobs – Icalc.

It is also known that unlike the above-mentioned monoclinic→cubic polymorphic transition, cubic CDP's conversion to Cs pyrophosphate ($Cs_2H_2P_2O_7$) above T_s is irreversible, i.e. cooling back down to RT under any conditions is not going to lead to the re-formation of any CDP polymorph. Consequently, RT XRD measurements and analysis can reveal if any chemical modifications via dehydration have occurred in a CDP sample previously heated above T_s. Figure 14 (a) shows a Rietveld refinement against XRD data collected at RT form the CDP powder used to press the pellet used in our impedance time-resolved impedance spectroscopy studies (the corresponding $P2_1/m$ structure is shown in the inset), whereas Figure 14 (b) shows similar data and analysis but from a powder obtained by grinding the pellet after being kept at 260°C in sealed dry air (22%rh) for 40h. The comparison between the two XRD patterns – in figures 14(a) and 14(b) – and the corresponding Rietveld refinements show that they are nearly identical, which unambiguously demonstrates that CDP sealed in dry air at 260°C <u>does not dehydrate</u> for at least 40h.

4) Our other important findings are related to the second major goal of the project: *to synthesize composite materials based on phosphate solid acids and highly dispersed oxides, and to investigate the crystal structures, proton conduction mechanisms, and thermal stability of their superprotonic phases.*

We have synthesized a CDP/SiO_2 composite that exhibits a proton conductivity significantly greater than that of pure CDP at T=260°C <u>in open air</u>. As shown in Figure 15, the proton conductivity of a 80% CDP / 20% SiO_2 composite measured in air at T=260°C decreases from $\sim10^{-2}$ to $\sim10^{-3}$ $S\cdot cm^{-1}$ over a 10h period, but is still nearly two orders of magnitude greater than that of pure CDP. A proton conductivity of $\sim10^{-3}$ $S\cdot cm^{-1}$ is obviously not enough to functionalize this composite as a fuel cell electrolyte, but our result confirms one of the main hypotheses of our project, namely that mixing CDP (or other superprotonic solid acids) with highly dispersed oxides such as SiO_2 is in fact an effective means to increase the proton conductivity at temperatures above the solid acid's superprotonic transition point.



<u>Figure 15</u> A significant proton conductivity increase over pure CDP was achieved (in an open atmosphere) by using CDP/SiO_2 composites.

Finally, we measured the time dependence of the proton conductivity of pure CDP *and* mixed 80% CDP / 20% SiO_2 composite in air and under high humidity conditions. Figure 16 (a) shows the σ vs. t dependence measured on CDP under air (squares) and high humidity P_{H2O}=0.38 atm. (circles). These data show that the superprotonic conduction is highly stable under humid conditions, i.e. σ ~ 10^{-2} S·cm^{-1} changes very little over a 10 h timespan. On the other hand, carrying out the time-resolved measurements in air reveals a rapid decrease of σ by more than two orders of magnitude over 10 h, as expected. Similar measurements performed on the 80% CDP / 20% SiO_2 mixed compound are shown in Figure 16 (b). In this case we observe that even under humid conditions σ exhibits a decrease from ~10^{-2} S·cm^{-1} to ~ 4×10^{-3} S·cm^{-1} over a 10 timespan. In addition, we note that the sample environment (dry or humid) matters little once nano-silica is added and the dry (squares) and humid (circles) "runs" almost overlap, as opposed to the case of neat CDP. This further demonstrates the strong effect of dispersed oxides on the superprotonic conduction of solid acids. While the microscopic aspects responsible for this behavior are most likely related to the desiccant properties of SiO_2, they are not fully understood and more micro- and meso-structural investigation of CDP / SiO_2 compounds is needed.

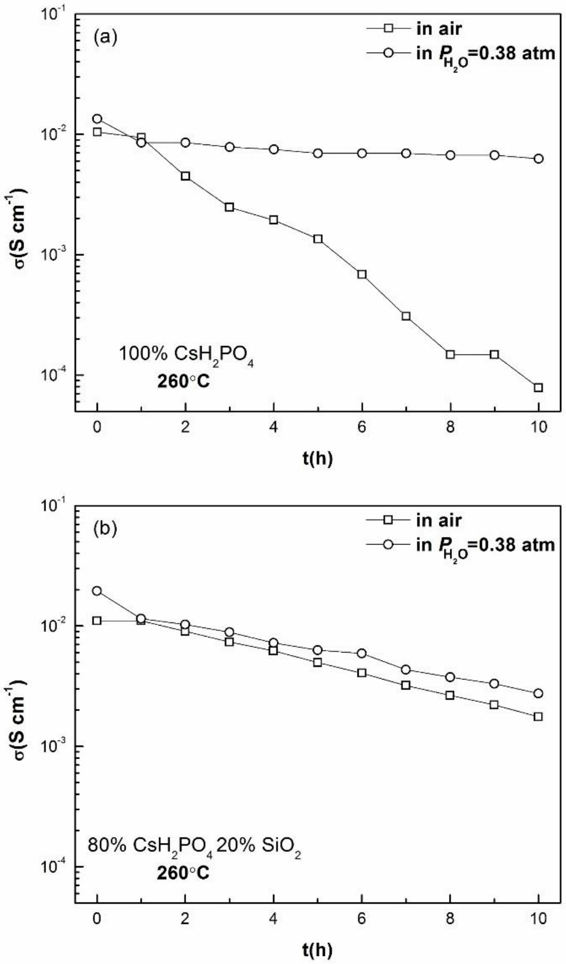


Figure 16 Time dependence of the proton conductivity measured on (a) 100%CDP and (b) 80%CDP/20%SiO_2 under air (squares) and humid (P_{H2O}~0.38 atm) (circles) conditions.