

# Structure and Dynamics Investigation of Barium Hydrogen Phosphate BaHPO<sub>4</sub>

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## Abstract

From a material design perspective, phosphates offer nearly limitless possibilities for various applications, including ion-exchange materials, solid electrolyte for batteries, linear and non-linear optical components, chelating agents, synthetics replacements for bone and teeth, phosphors, detergents, and fertilizers. As a consequence of its thermal and chemical properties, Barium Hydrogen Phosphate (BaHPO<sub>4</sub>) plays an important role in catalytic chemistry, industrial paint manufacturing and ink-related charge direction. Because hydrogen and hydrogen bonds significantly affect these properties, studying proton mechanisms such as proton diffusive motions and jumps is critical to developing a comprehensive understanding of the compound, allowing further determination of potential applications. Here, we utilize incoherent Quasi-Elastic Neutron Scattering (QENS). QENS is a useful technique to determine diffusive motions in the 10-12 to 10-9 second time range at length scales from 3 Å to 60 Å, which apply to hydrogen ion diffusion and hydrogenous species. Protons have a substantial neutron cross section, which subsequently enhances the associated QENS signal, and permits studies of low-proton systems such as BaHPO<sub>4</sub>. The QENS investigation was conducted using 7 discrete temperatures ranging from 293 to 573 Kelvin, while subsequent fitting and analysis revealed the diffusion coefficient as a function of temperature. Obtained results for BaHPO<sub>4</sub> were compared to Monetite (CaHPO<sub>4</sub>). In addition to QENS, data from Neutron Powder Diffraction (NPD) using Linear Position Sensitive Detector (LPD) was analyzed to further comprehend the crystal structure of BaHPO<sub>4</sub> and to check its consistency. Lastly, images from Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) provided support by giving insight to the surface topography of the sample to allow us to analyze the feasibility of BaHPO<sub>4</sub> as potential application for other fields.

## Experiment Methods

The sample of Barium Hydrogen Phosphate (BaHPO<sub>4</sub>) was in powder form when carried out the following studies.

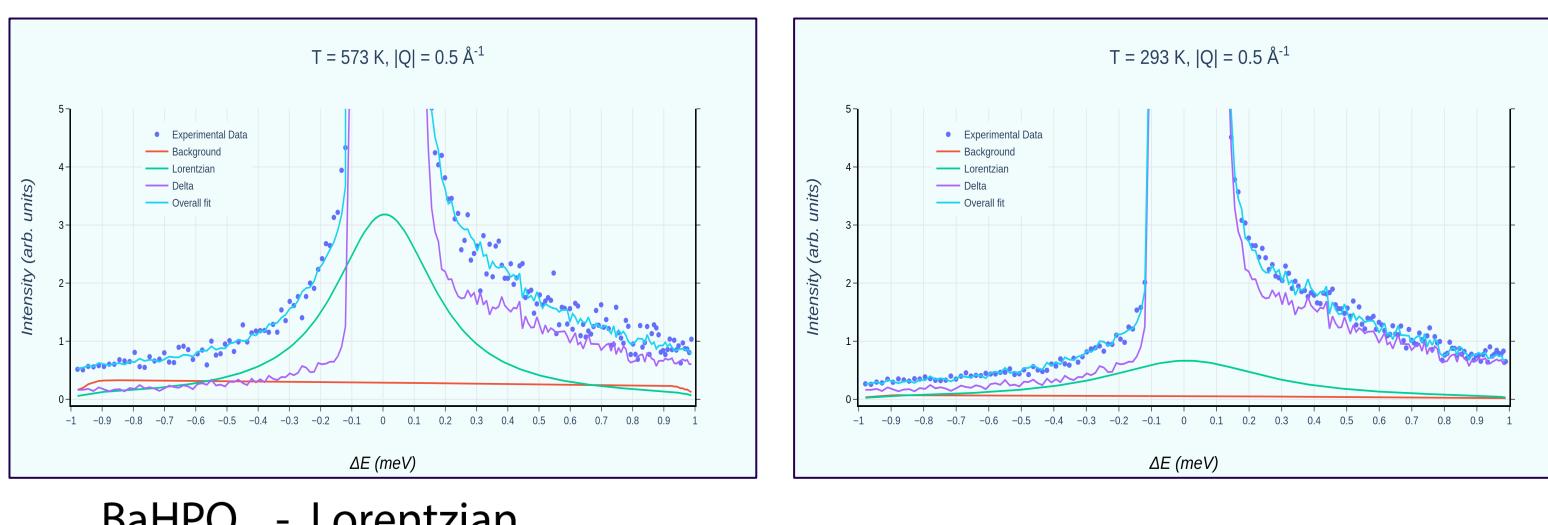
Quasi-Elastic Neutron Scattering (QENS) study was performed on the sample by the Disk Chopper Spectrometer (DCS) located at the National Institute of Standards and Technology (NIST) center for Neutron Research in Maryland, United States. The DCS produces a cleanpulsed monochromatic neutron beam using its seven disk choppers with incident wavelengths ranging from ~0.23 to ~0.23 nm (~2.3 to ~10 Å).

Neutron Powder Diffraction (NPD) was performed using the PSD powder instrument located at the Missouri University Research Reactor (MURR), which utilizes five vertically stacked Linear Position Sensitive Detectors (LPD). The instrument wavelength is  $\lambda = 1.485\text{Å}$  and uses Si (511) crystal monochromator. Furthermore, the instrument has resolution of  $1.5 \times 10^{-3} (\frac{\Delta d}{d})$ .

## QENS Analysis

QENS fitting:

- Performed at 7 temperatures
- Consists of Delta curve convoluted with Lorentzian curve
- Lorentzian curve yields information regarding dynamics
- Fitting performed using DAVE software suite
- A Diffusive process may be indicated by increasing width of the Lorentzian curve with both momentum transfer and temperature
- Fig. 3 shows a clear increase in the Lorentzian width with temperature
- Fig. 1.2 at the bottom compares the overall fitting of the lowest and highest temperatures (293K and 573K, respectively)

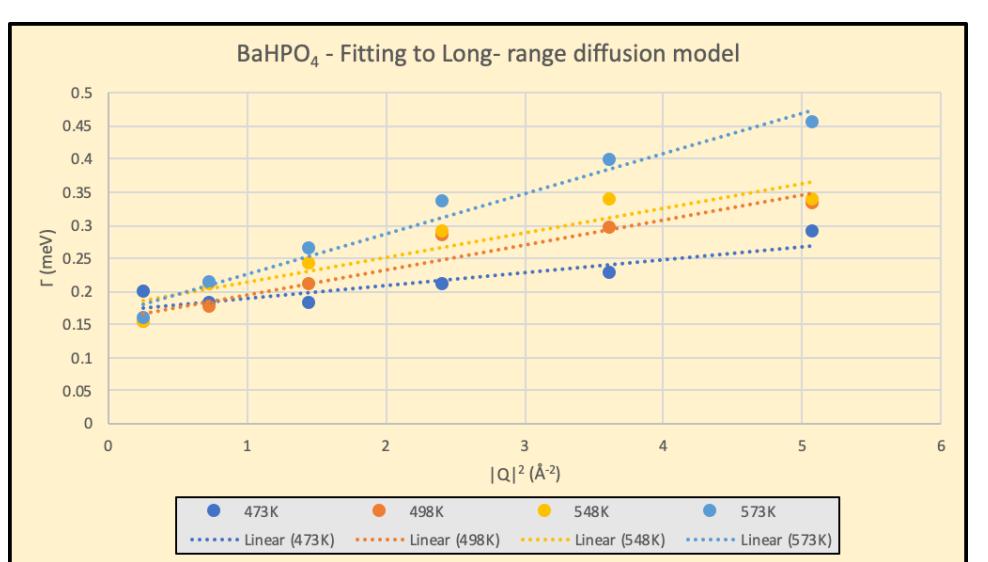


TOP LEFT: Fig. 1 - The Fitting procedure for 573K at  $|Q|=0.5\text{ \AA}^{-1}$   
TOP RIGHT: Fig. 2 - The fitting procedure for the 193 at  $|Q|=0.6\text{ \AA}^{-1}$   
LEFT: Fig. 3 - the Lorentzian contributions of the fitting for all temps at  $|Q|=0.5\text{ \AA}^{-1}$

## QENS to probe Proton dynamics

- Various diffusion models exist for proton dynamics in a solid
- Models for short, intermediate, and long range diffusion
- Research is still ongoing, but initial fitting to the long-range diffusion model is included below

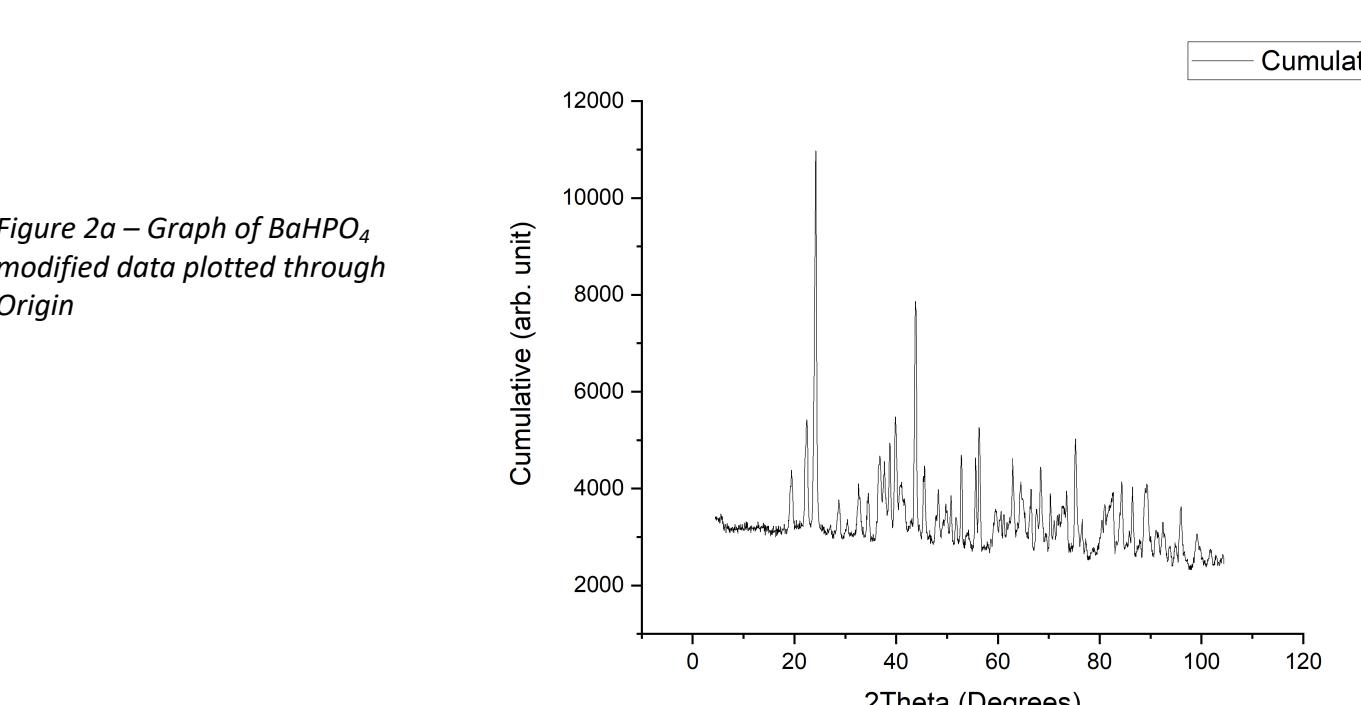
Temperature (K)	Diffusion Coefficient (cm <sup>2</sup> /s)
473	3.00711E-06
498	5.72928E-06
548	5.71696E-06
573	9.2652E-06



## NPD Analysis

Neutron Powder Diffraction (NPD) analysis gives us a valuable insight to the crystal structure of Barium Hydrogen Phosphate. X-Ray Diffraction analysis (XRD) and NPD are often compared and argued that one could do another's job. However, we chose to study BaHPO<sub>4</sub> with NPD instead of XRD. Since the NPD data gives detail information about the light atoms. Thus, by studying NPD data we can accurately know the Oxygen and Hydrogen atom positions to check for consistency with the QENS analysis results.

After the raw data was collected. It was plotted through the software, Origin Pro, to view the figure and spot any inconsistencies or any possible detector malfunction. After removing any inconsistencies, we export the modified data to the FullProf software. Figure 2a shows the raw data plotted through Origin. After the modified data has been uploaded to FullProf, number of parameters were specified to fit the data to Thompson-Cox-Voigt function. Figure 2a shows Intensity of the diffraction. Even though, we are midway through the NPD analysis, the future step is to incorporate Rietveld Refinement method to further refine the data to further characterize the BaHPO<sub>4</sub> crystal.



Crystal Structure of Barium Hydrogen Orthophosphate

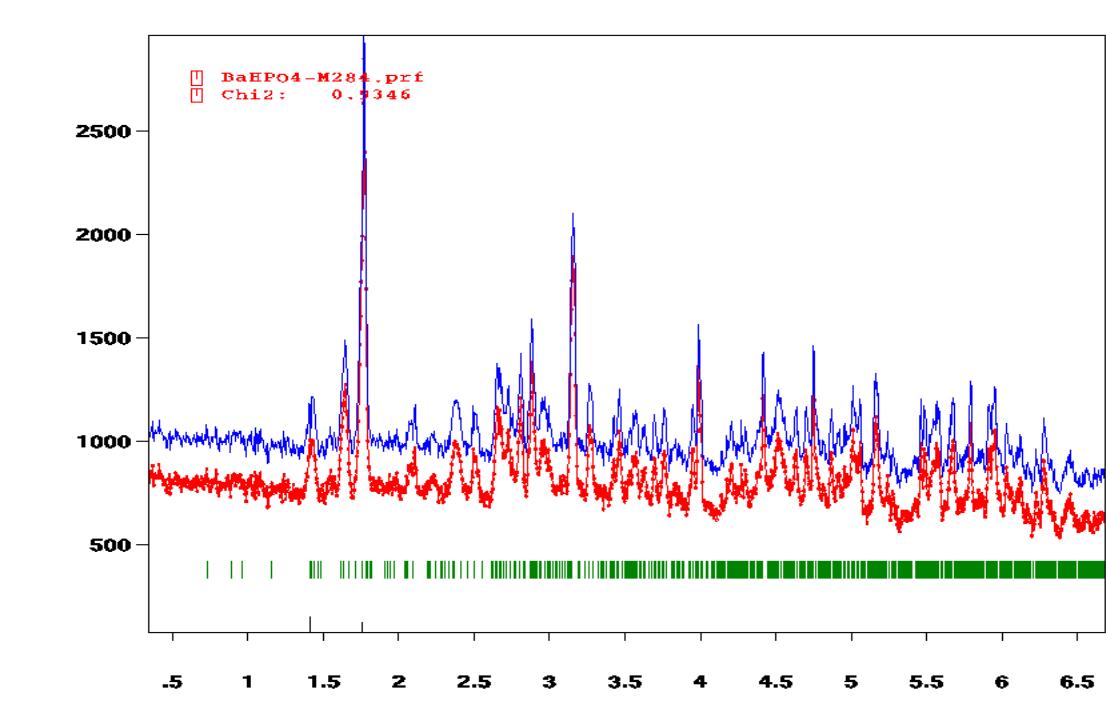
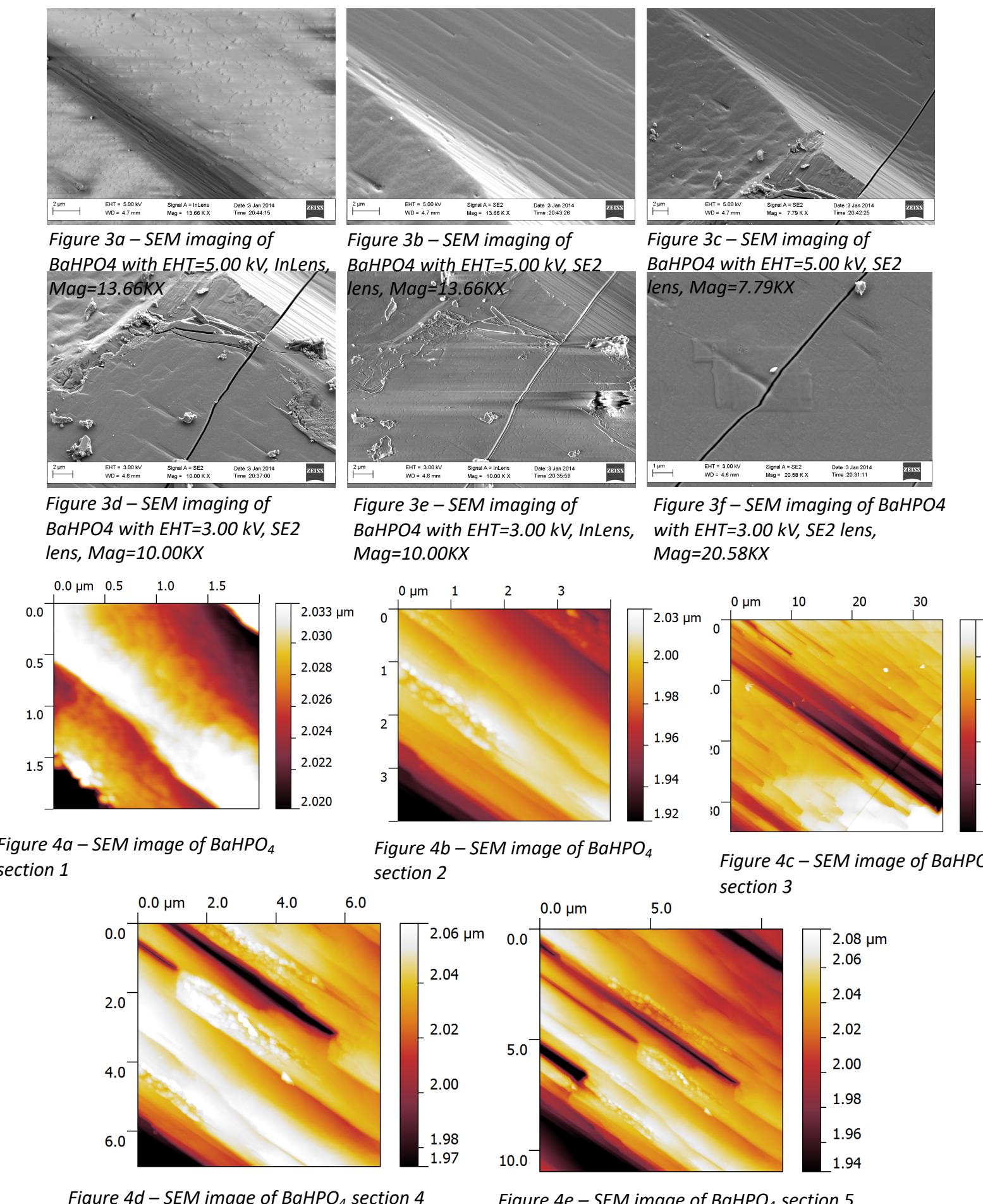


Figure 2b – Graph of BaHPO<sub>4</sub> data plotted through FullProf

## AFM and SEM Study



## AFM and SEM Analysis

Atomic Force Microscopy (AFM) and Scanning Electron Microscopy are techniques used to further understand BaHPO<sub>4</sub> by obtaining images of their surface topography. Surface topography is crucial because the surface topography could be linked to the proton conductivity. Even though, we have obtained the images, our investigation into surface topography is still ongoing. Above images are the AFM and SEM images we obtained. In the future we will study the AFM surface topography as function of temperature.

## Acknowledgement

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