CHARACTERISING ANTI-PEROVSKITE SOLID ELECTROLYTES

Using AFM to explore the properties of Li_2OHX systems

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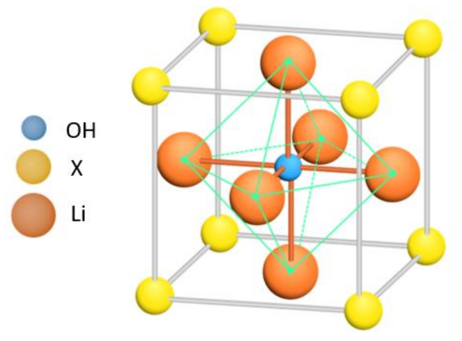
INTRODUCTION

With the increased demand for **renewable** energy sources, **solid state** lithium metal batteries (SSLMBs) could pave the way for the future of energy storage. They offer several **advantages** over liquid electrolyte batteries, primarily[1]:

- Safety
- Higher energy density
- Longer life cycle
- Wider operating temperature range



Lithium hydroxyhalide anti-perovskites (Li_2OHX, X = Cl, Br) are good candidates for the solid electrolytes required in these batteries due to their **ionic conductivity**, **chemical inactivity** when in contact with lithium and their **low melting points** (≈300°C) which allows for **dense** samples to be produced in a **single step**, with the grain size **controlled** through the cooling rate. This is important as **porosity** and **grain boundaries** can lead to inhomogeneous lithium **deposition**[2].

Atomic force microscopy (AFM) was used to image these solids, capable of mapping the **topography** and **mechanical properties** simultaneously.

MOTIVATION

- Characterising the microstructure and properties of Li_2OHCl and Li_2OHBr helps to understand the **phase diagrams,** guiding future synthesis
- This could help in the design of **future batteries** using these solid electrolytes

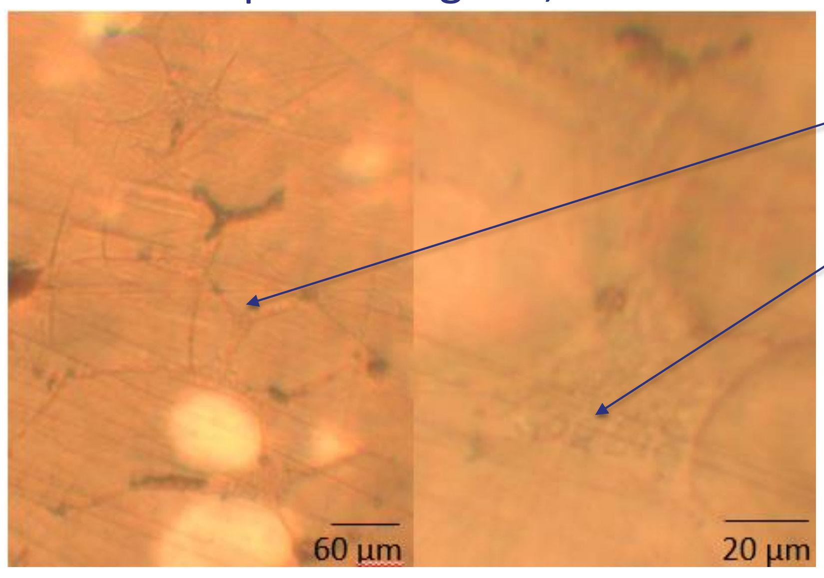
METHODS

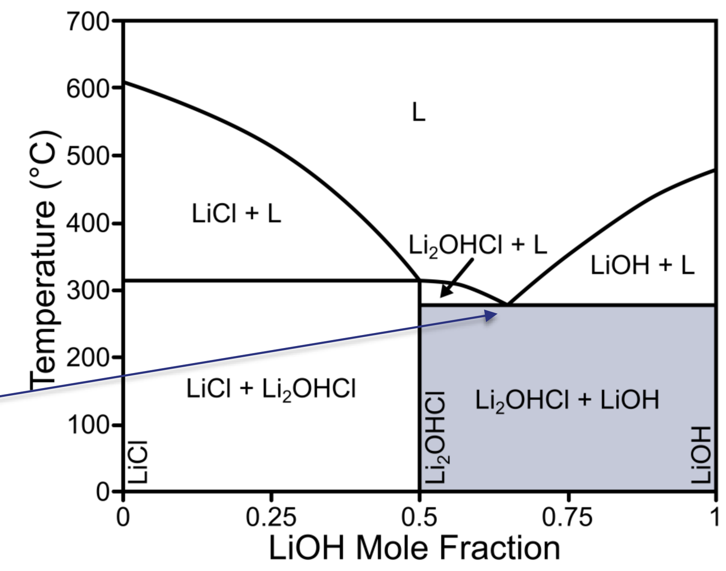
- **Pellets** of each bromide and chloride, synthesised with a slight excess of LiOH (1:1.07, LiX:LiOH, due to seeing large impurities in the XRD for 1:1)[3], were set in an **epoxy resin** and **polished** using grinding papers in an argon filled glovebox
- The samples were then imaged using an **optical microscope**
- The **AFM** was **calibrated** to give the tip radius, deflection sensitivity and spring constant of the cantilever enabling accurate force determination during imaging
- PeakForce Quantitative Nanomechanical Mapping (**PF-QNM**) was employed[4] to measure very fast force-displacement curves at **every pixel**, with the retract curves used to calculate the **elastic modulus** of each sample (using the **same** imaging conditions) whilst the **height** was simultaneously mapped. Further information about **AFM** can be found **here.**

OPTICAL MICROSCOPE IMAGES

CHLORIDE

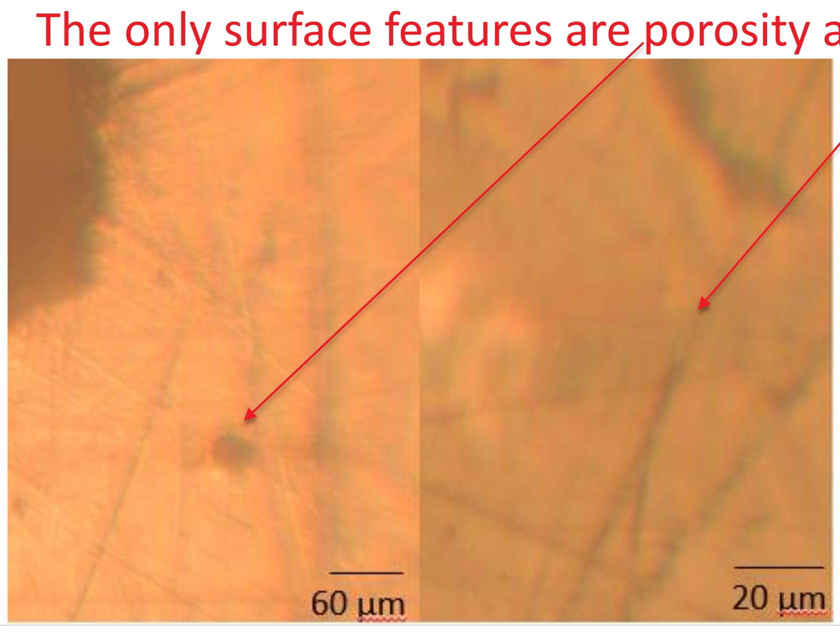
- The polishing process revealed a dendritic microstructure with **eutectic regions**
- From the phase diagram, the **secondary phase** is expected to be **LiOH**



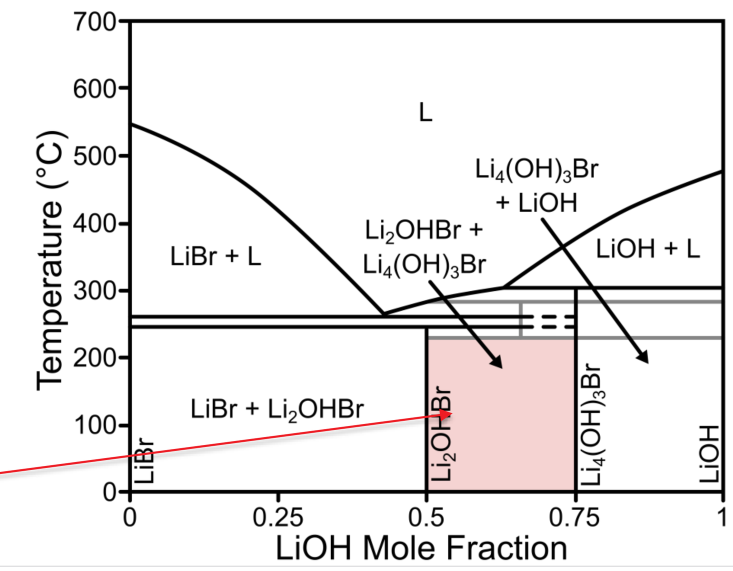


BROMIDE

- There is no evidence for **impurity phases**
- The only surface features are porosity and scratches (from the polishing)

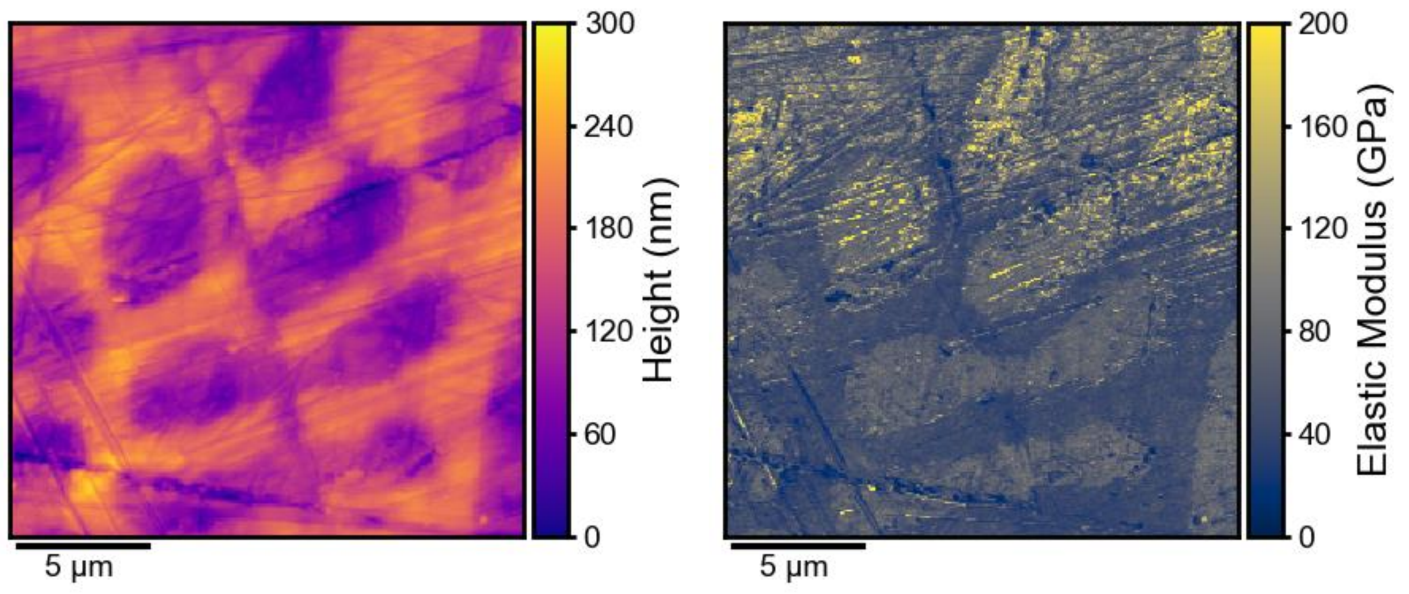


The phase diagram is more complex and not fully understood, the reaction doesn't pass through a eutectic point and so eutectic growth is not expected.



PF-QNM IMAGES: HEIGHT AND MODULUS MAPPING

CHLORIDE



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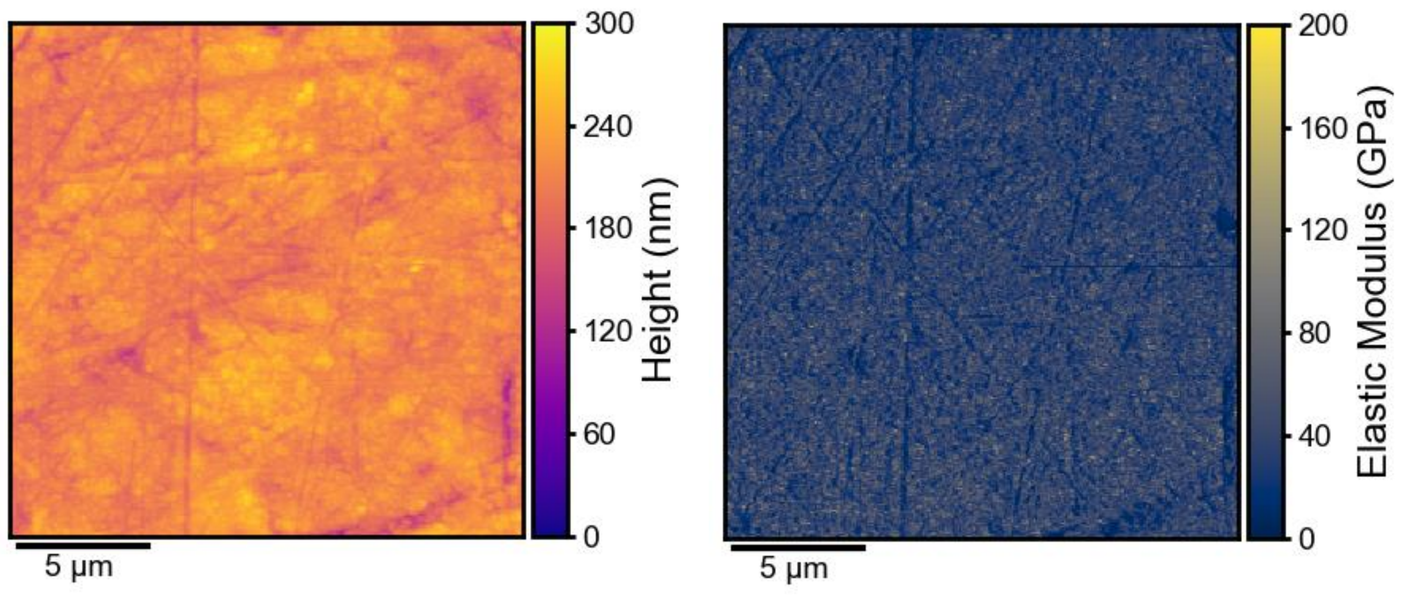
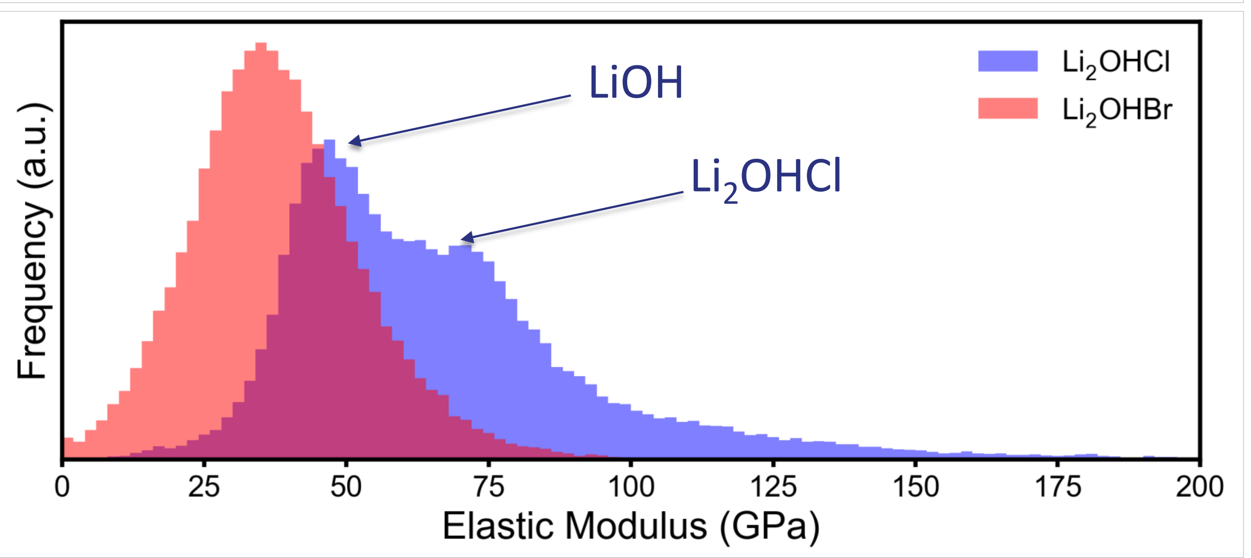


CONCLUSIONS

- A **two phase eutectic region** is shown in both the height map and modulus of the chloride sample, which is further evidenced by the modulus distribution plot showing **two peaks** for the chloride (one for each phase)
- The bromide sample appears to be a **single phase** in this region as shown by the **single peak** in the plot
- The chloride sample has a **higher modulus** in the anti-perovskite phase (the peak at about 70 GPa) compared to the bromide (peak at 35 GPa)



IMPACT / NEXT STEPS

- The difficulty of the synthesis of these **pure** solid electrolytes is often overlooked, and for the chloride there are multiple eutectic regions with **impurities** of LiOH (which will have **impacts** on the **ionic conductivity** and **performance** of the battery)
- The reactions during the synthesis of the bromide are **complicated** so **further work** should be done to identify the composition and **elucidate the phase diagram**
- A consideration of the **mechanical properties** of these solid electrolytes is important in the design of SSLMBs[5]
- Further synthesis pathways should be explored to **minimize** these impurities, which will be **crucial** if these solid electrolytes are to be used in the **future of SSLMBs**

REFERENCES

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- 5. Pasta, M. *et al.* 2020 roadmap on solid-state batteries. *JPhys Energy* **2**, (2020).

INTERN BIO

Alex is a 4th year Chemistry Undergraduate studying at the University of Oxford. He completed his Faraday FUSE Internship in the Pasta Group at the University of Oxford.

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