Proton conductivity of tin(IV) N,N-bis(phosphonomethyl)glycine phosphonates and their pyrophosphate-based derivatives

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Network for Sustainable Nanotechnology

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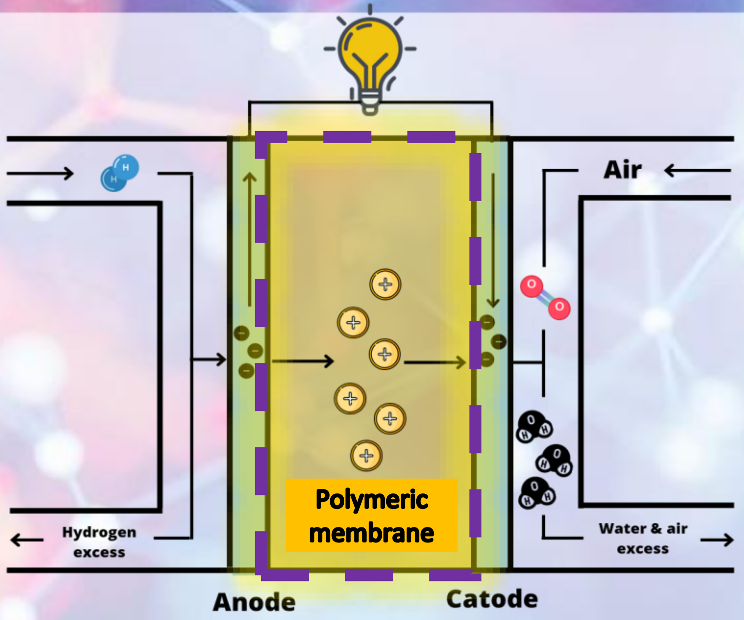
The need of a change

- Improving performances of Proton Exchange Membranes (PEMs) and Intermediate Temperature Fuel Cells (ITFCs)



Metal phosphonates (MPs)

I. Versatility in coordination environments
II. Use of abundant and low-cost metals (Sn, Zr, Ti …)
III. Easily tuneable properties modified by synthesis parameters
IV. Wide range of ligands with different functional groups

Metal Pyrophosphates (MPPs)

I. Conductivity depending on the treatment
II. High chemical and thermal stability
III. Core-Shell type structure conductivity with adjustable properties

→ **PROTON CONDUCTORS**

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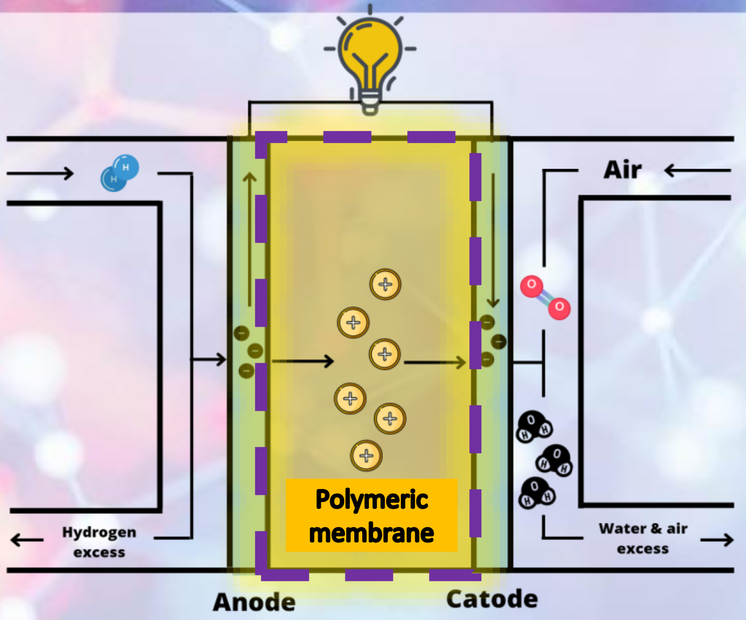

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Pyrolysis

Metal Pyrophosphates (MPPs)

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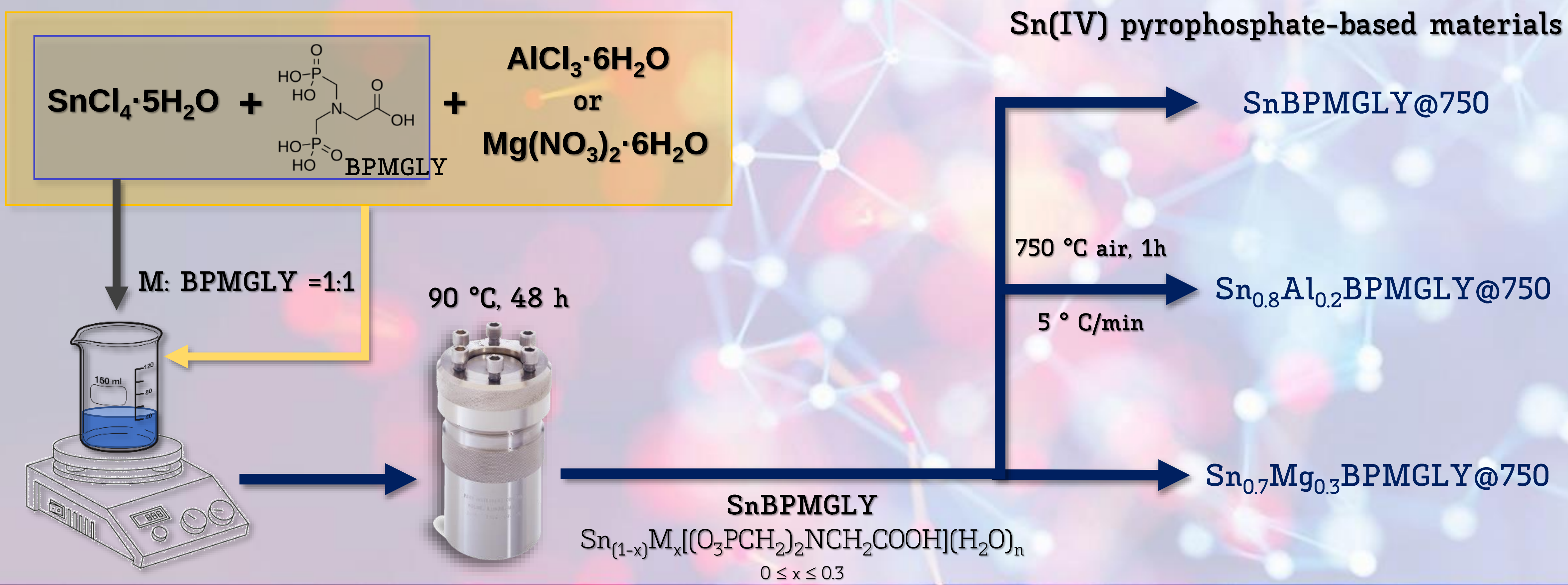
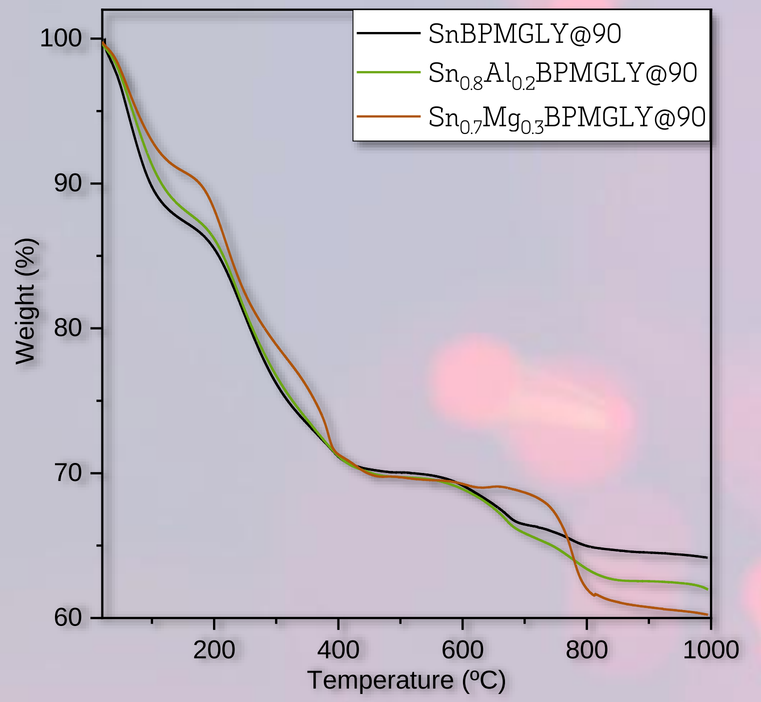
PROTON CONDUCTORS

Synthesis of Sn(IV)BPMGLY derivatives

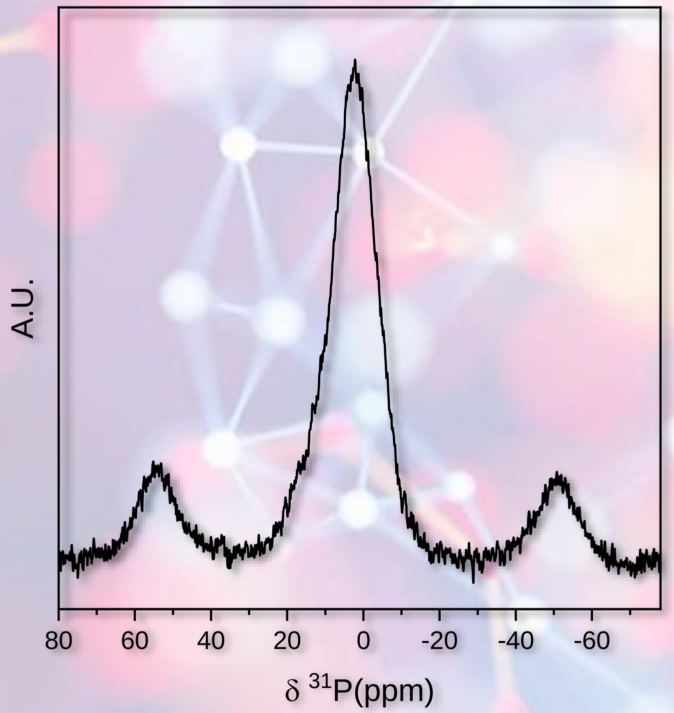


Characterization of the as-synthesized amorphous compounds: $Sn_{(1-x)}M_x[(O_3PCH_2)_2NCH_2COOH](H_2O)_n$

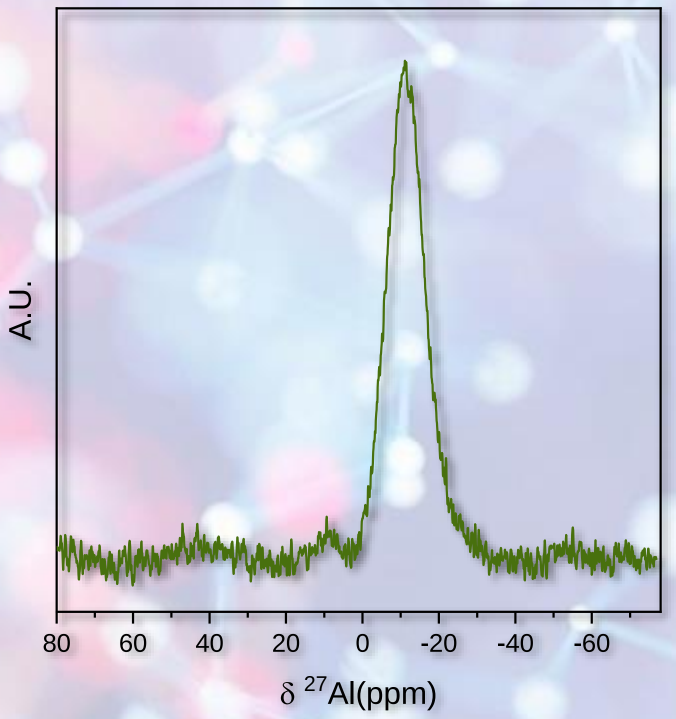
TGA



^{31}P MAS-NMR



^{27}Al MAS-NMR



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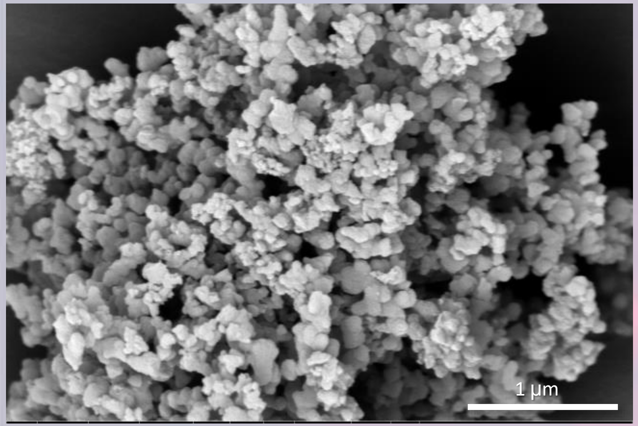
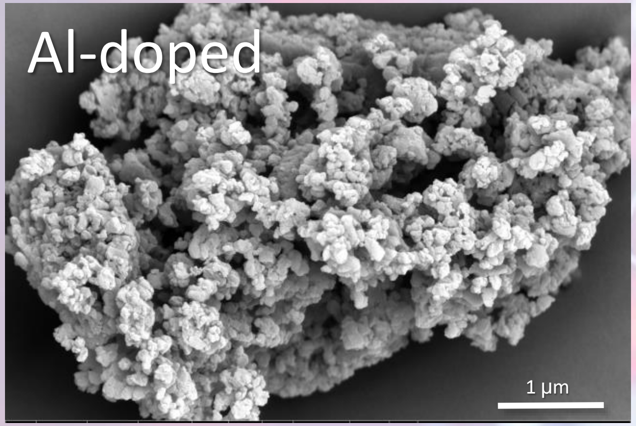
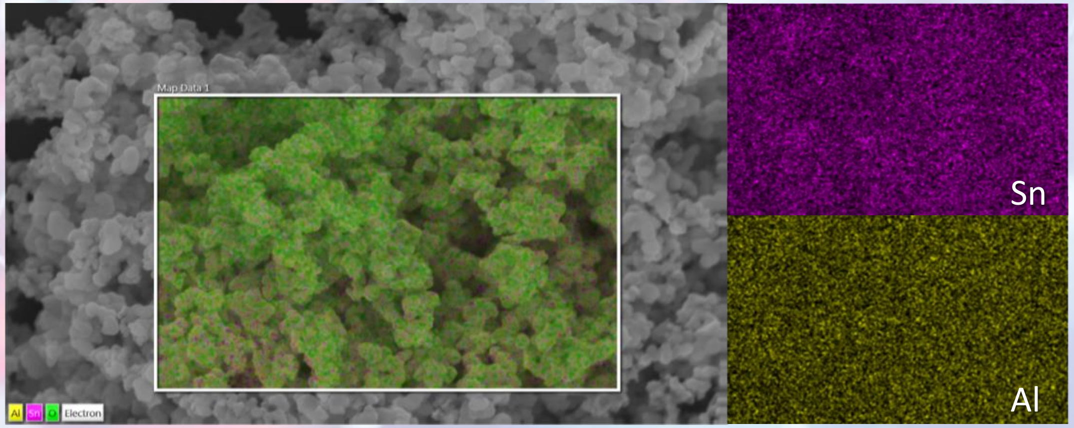
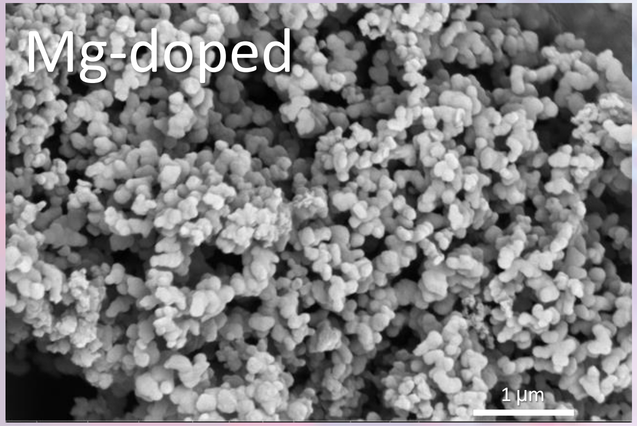
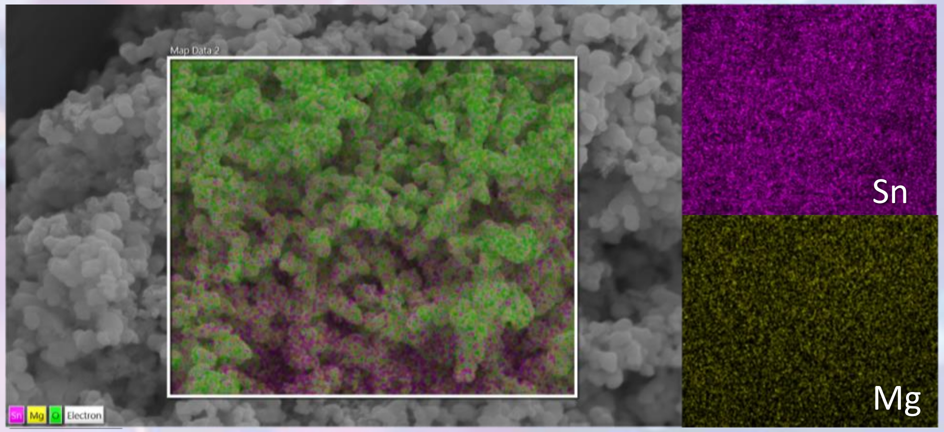
SEM-EDS





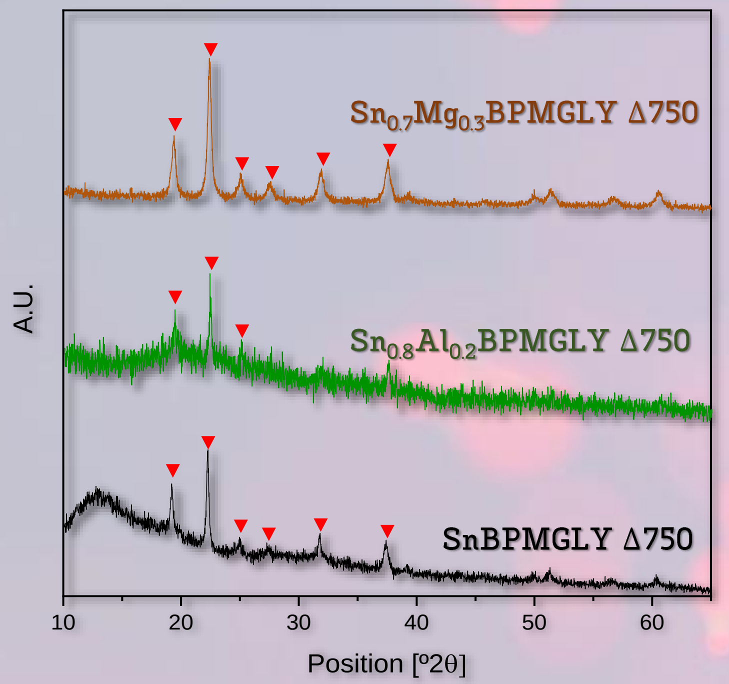






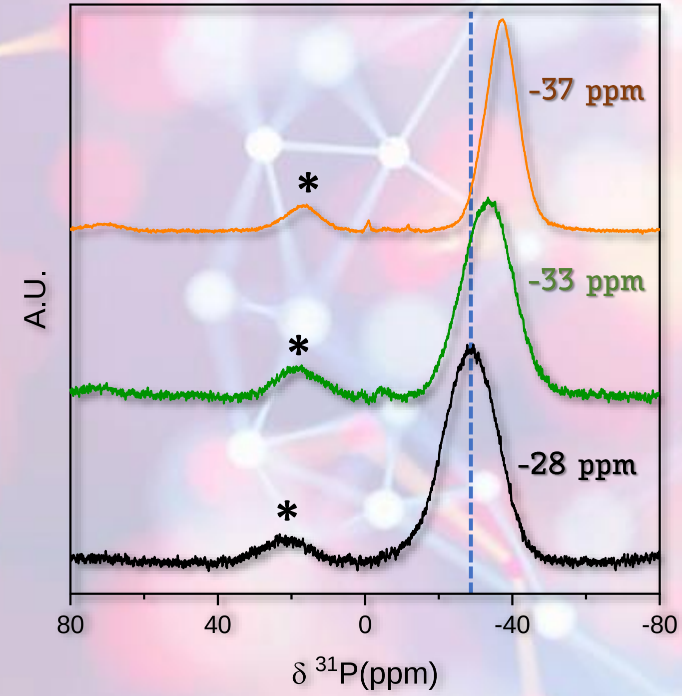
Characterization of pyrolyzed (750 °C, air) derivatives (SnBPMGLY Δ750)

X-ray powder diffraction data



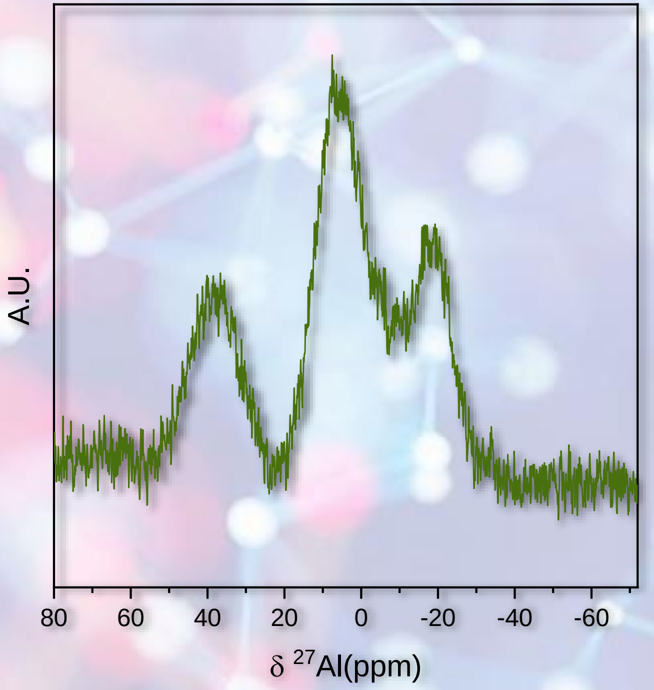
▼ SnP_2O_7

^{31}P MAS-NMR



*Sidebands

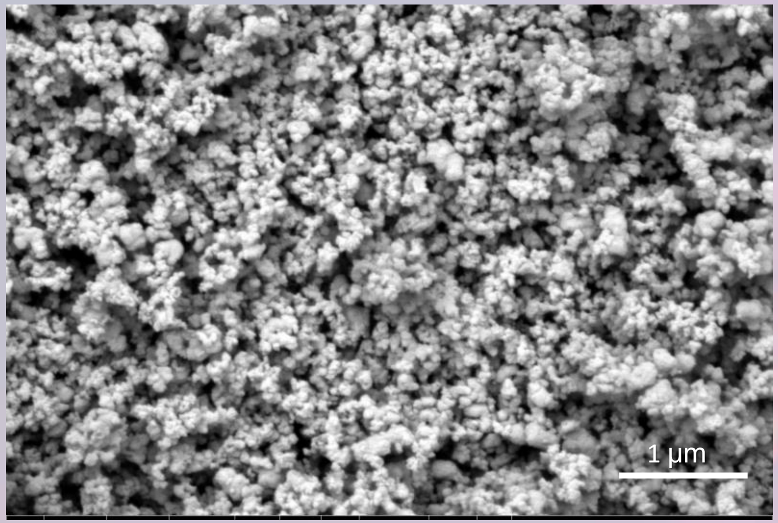
^{27}Al MAS-NMR



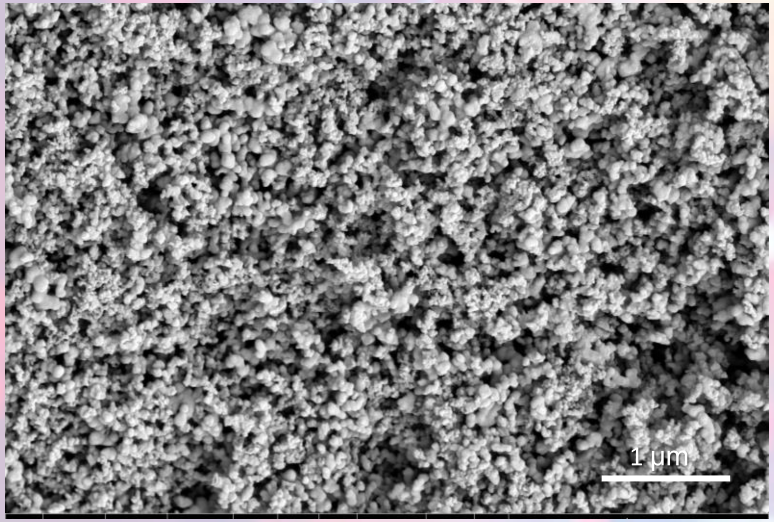
Pyrolyzed (750 °C, air) derivatives (M-doped SnBPMGLY Δ750)

SEM images

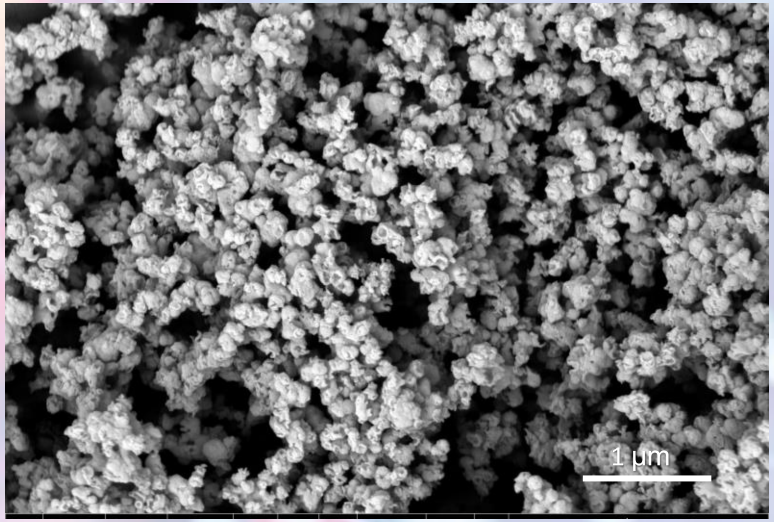
SnBPMGLY Δ750



$Sn_{0.8}Al_{0.2}$BPMGLY Δ750

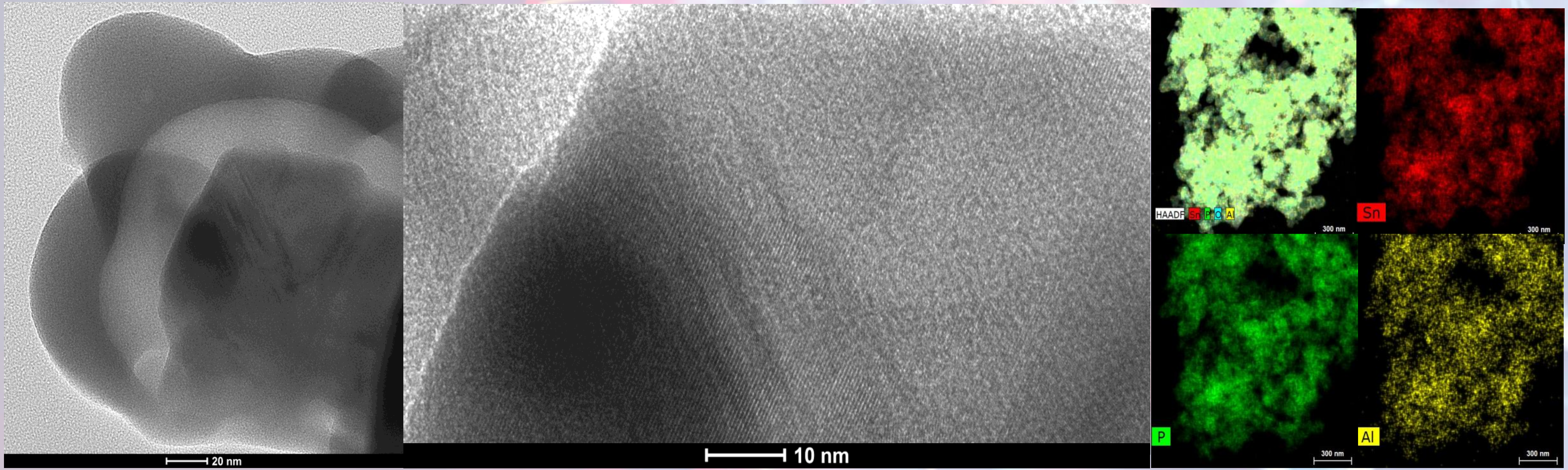


$Sn_{0.7}Mg_{0.3}$BPMGLY Δ750



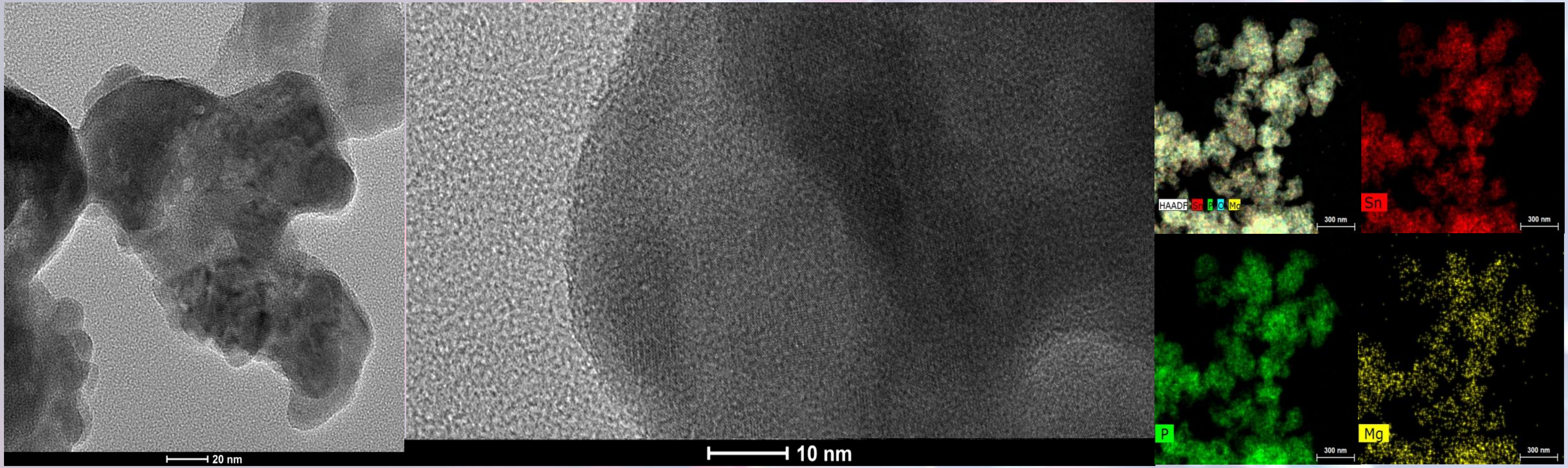
Pyrolysed derivatives (Al-doped SnBPMGLY Δ750)

- TEM-EDS for $Sn_{0.8}Al_{0.2}$BPMGLY@750



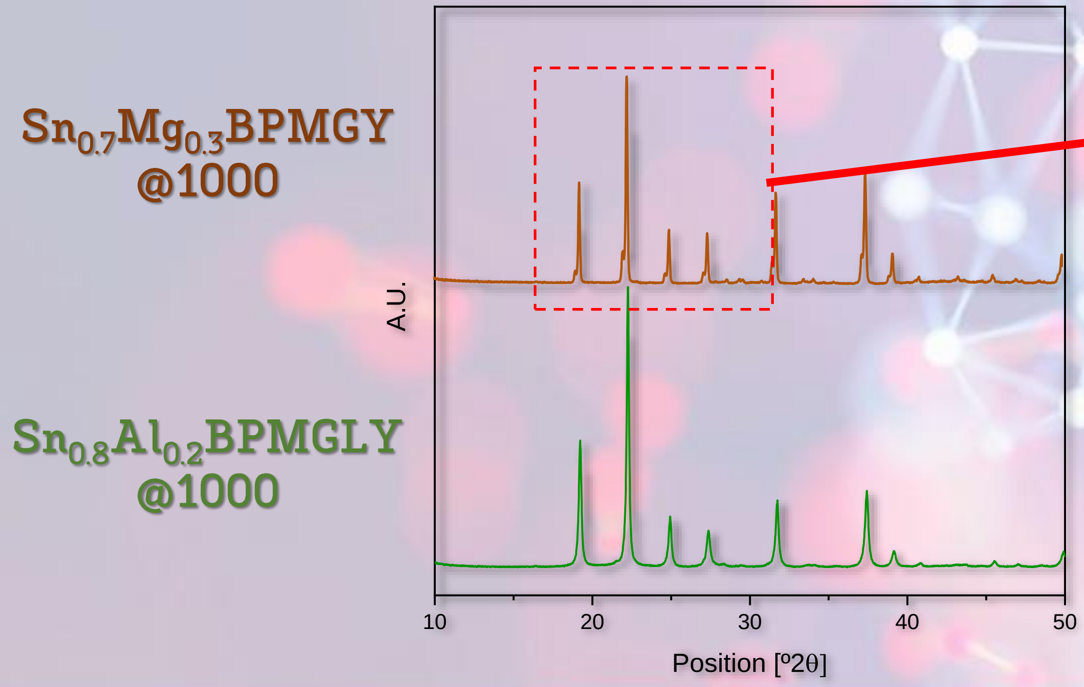
Pyrolysed derivatives (Mg-doped SnBPMGLY Δ750)

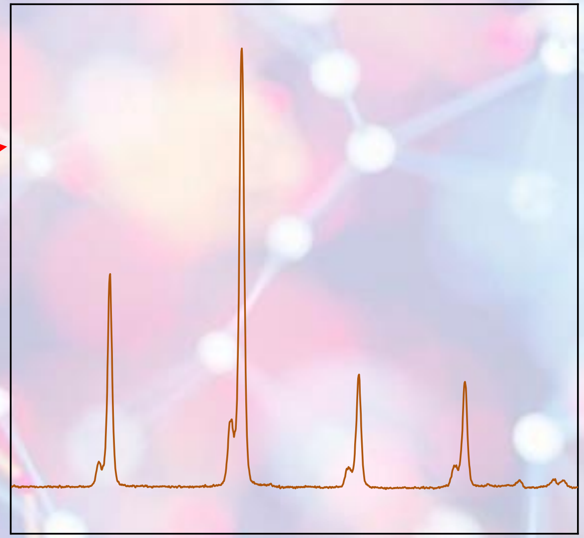
- TEM-EDS for $Sn_{0.7}Mg_{0.3}$BPMGLY Δ750



Pyrolysed derivatives (M-doped SnBPMGLY Δ1000)

X-ray diffraction patterns

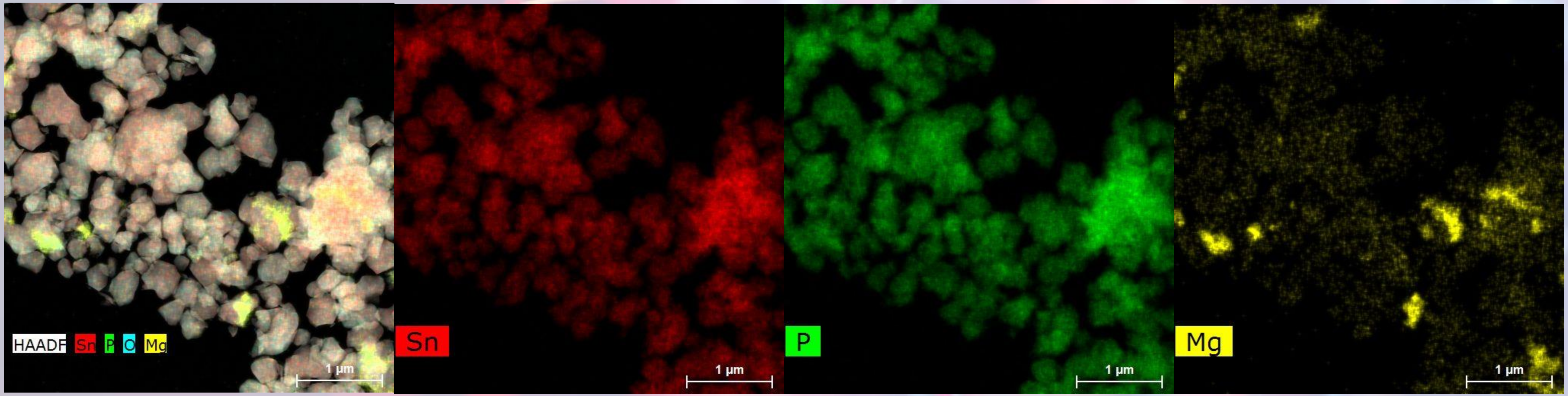




Phase segregation

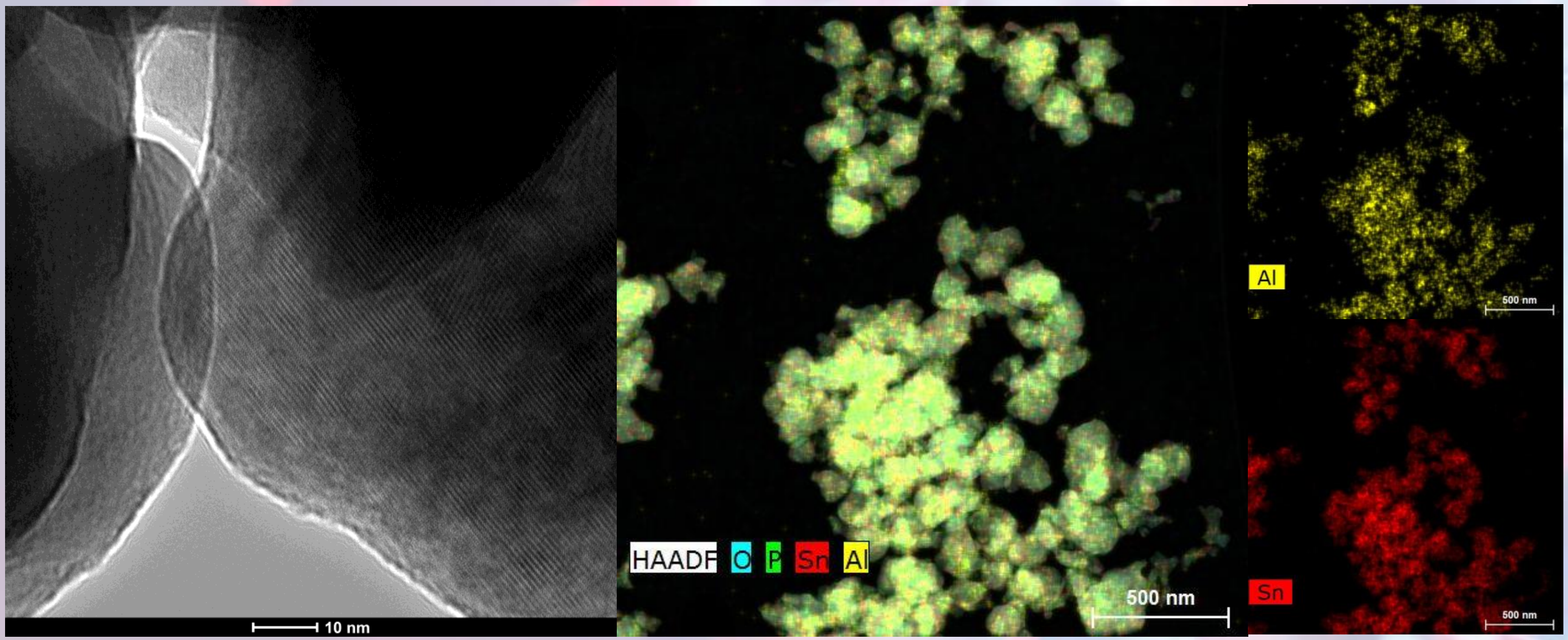
Pyrolysed derivatives (Mg-doped SnBPMGLY Δ1000)

- TEM-EDX images for $Sn_{0.7}Mg_{0.3}$BPMGLY Δ1000

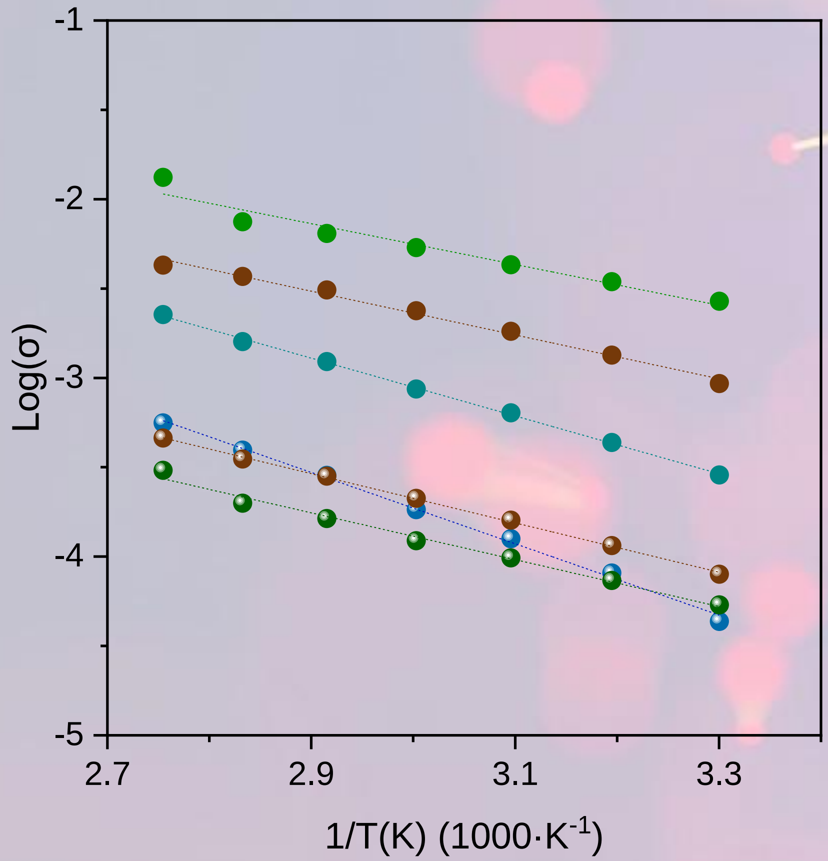


Pyrolysed derivatives (Al-doped SnBPMGLY Δ1000)

- TEM_EDX for $Sn_{0.8}Al_{0.2}$BPMGLY@1000

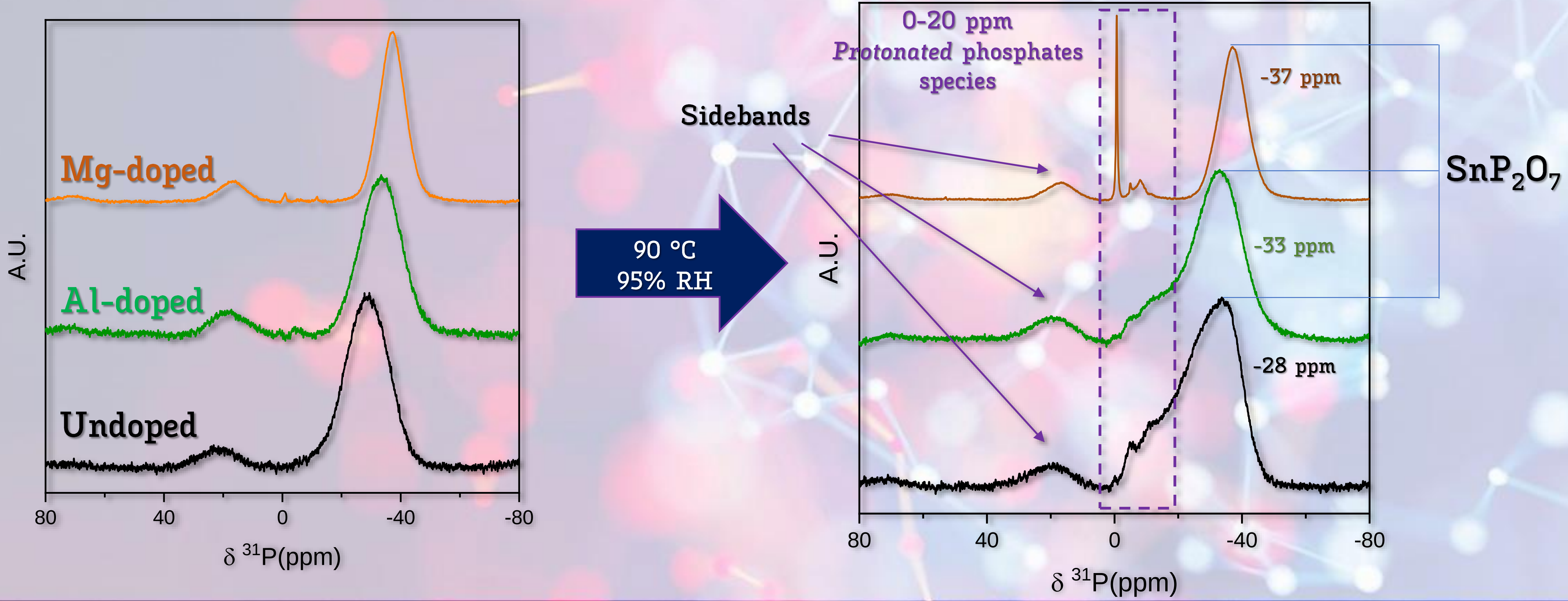


Proton conductivity properties



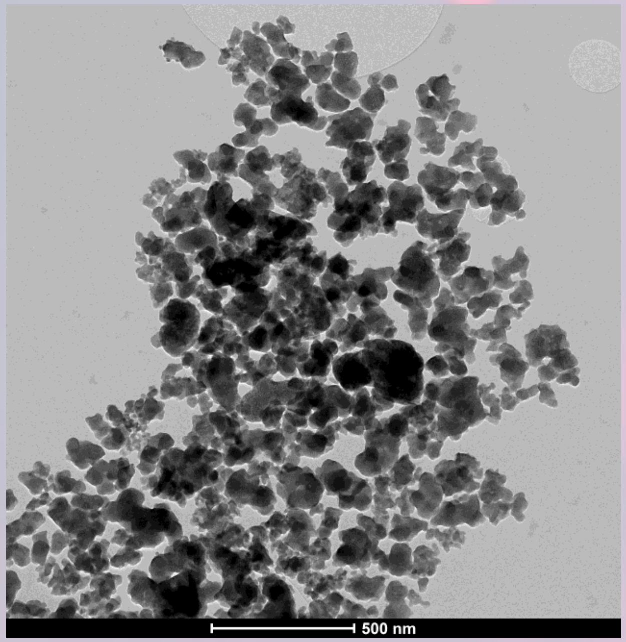
Sample	σ (S·cm^{-1})		Activation Energies (eV)
	90 °C, 95% RH	90 °C, 75% RH	95% RH
SnBPMGLY	$5.60 \cdot 10^{-4}$	$3.88 \cdot 10^{-5}$	0.326
$Sn_{0.8}Al_{0.2}$BPMGLY	$3.03 \cdot 10^{-4}$	$3.97 \cdot 10^{-5}$	0.259
$Sn_{0.7}Mg_{0.3}$BPMGLY	$4.60 \cdot 10^{-4}$	-	0.243
SnBPMGLY Δ750	$2.20 \cdot 10^{-3}$	$4.80 \cdot 10^{-4}$	0.316
$Sn_{0.8}Al_{0.2}$BPMGLY Δ750	$1.32 \cdot 10^{-2}$	$3.25 \cdot 10^{-3}$	0.226
$Sn_{0.7}Mg_{0.3}$BPMGLY Δ750	$4.28 \cdot 10^{-3}$	$9.99 \cdot 10^{-4}$	0.243

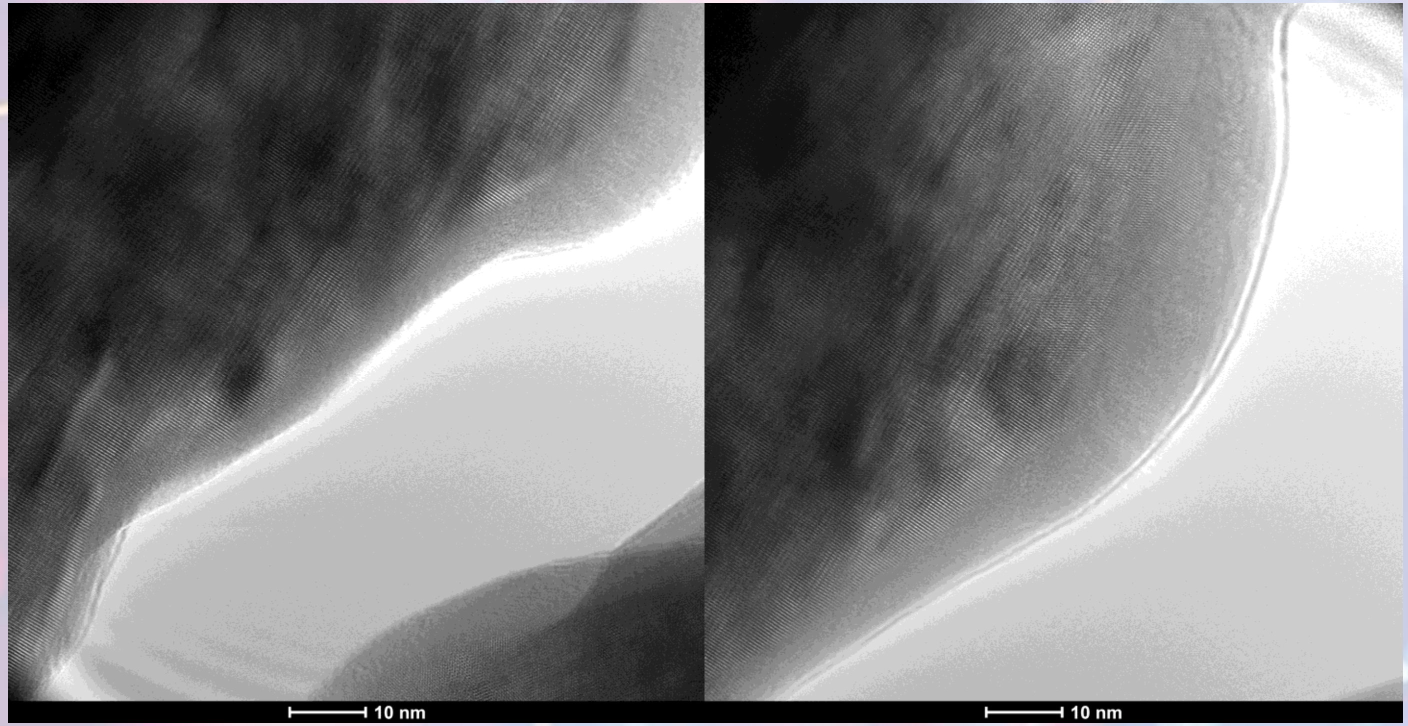
Post-impedance characterization: ^{31}P MAS-NMR study



Post-impedance characterization

- TEM of SnBPMGLY Δ750





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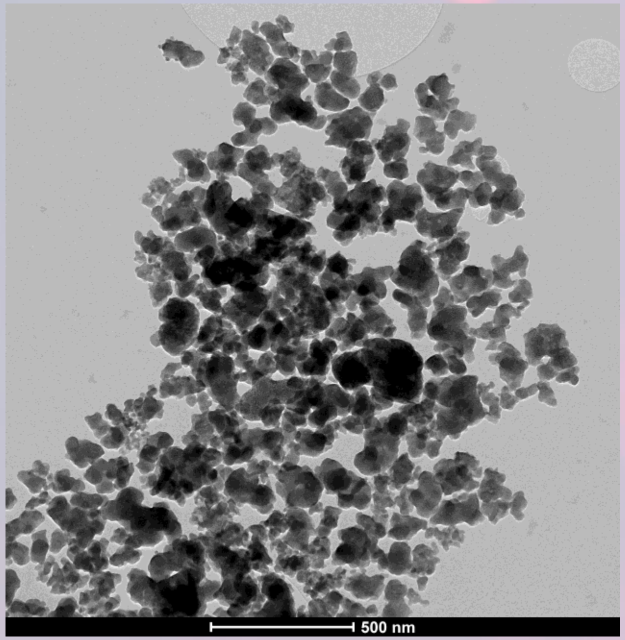
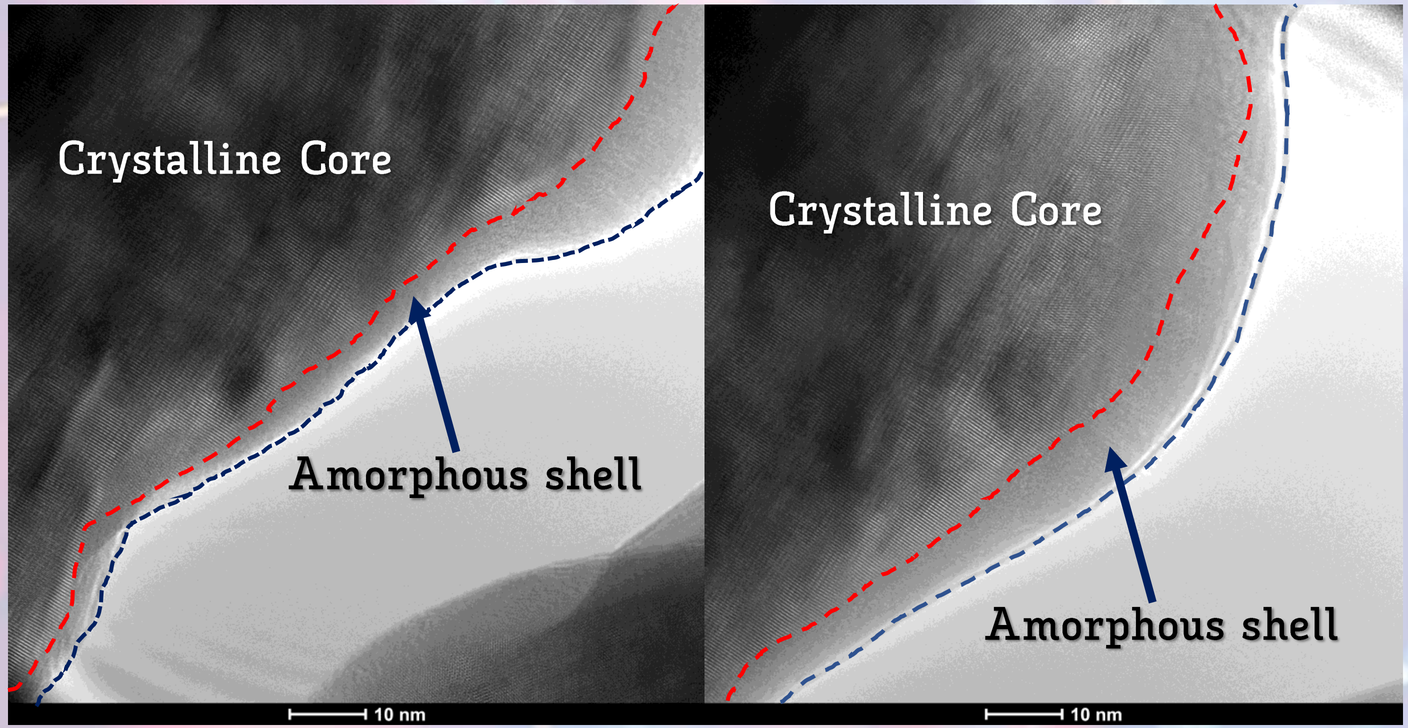
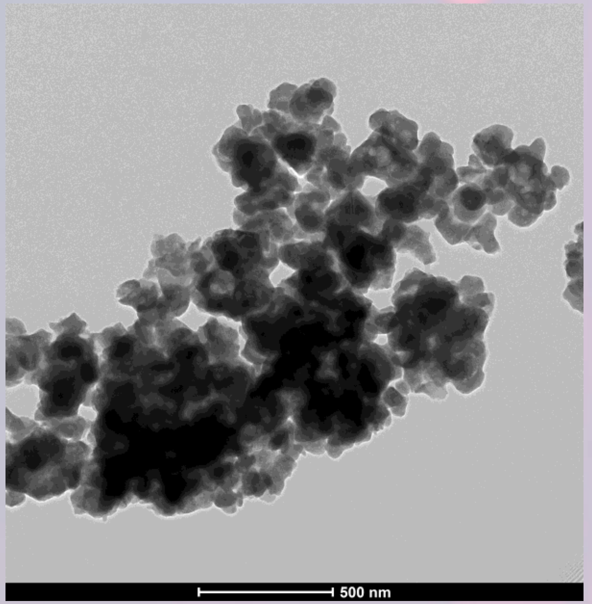
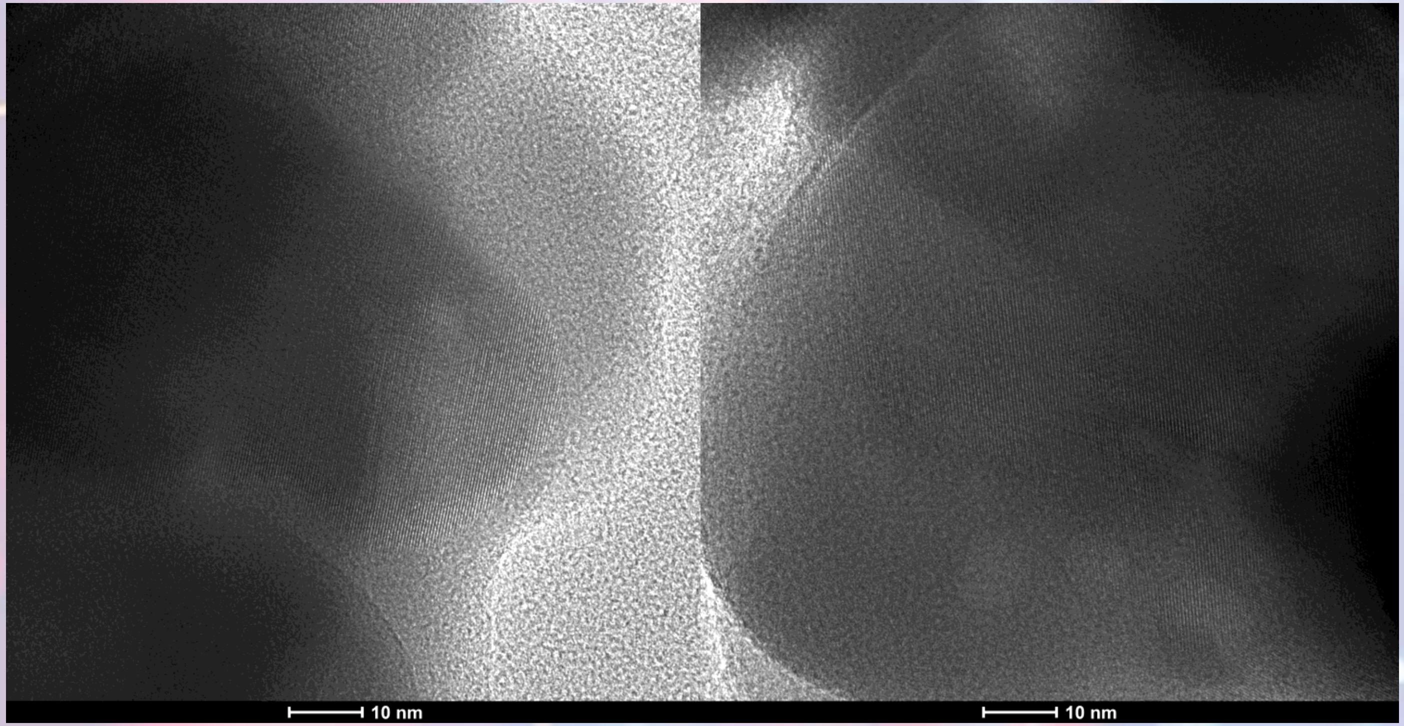




Post-impedance characterization

- TEM of $Sn_{0.8}Al_{0.2}$BPMGLY Δ750





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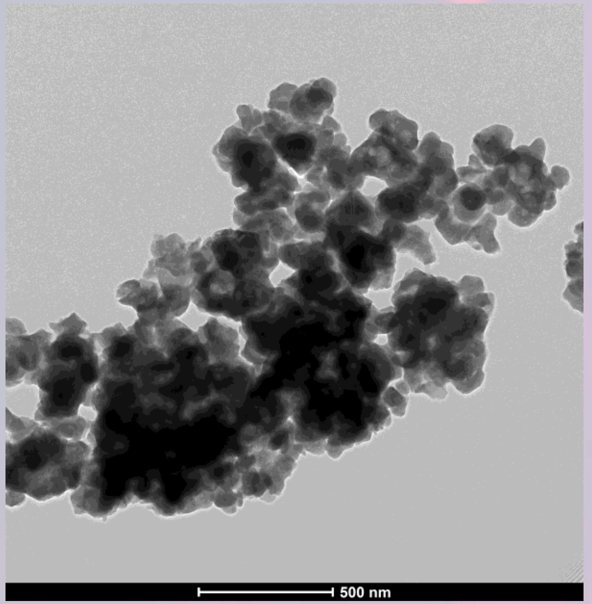

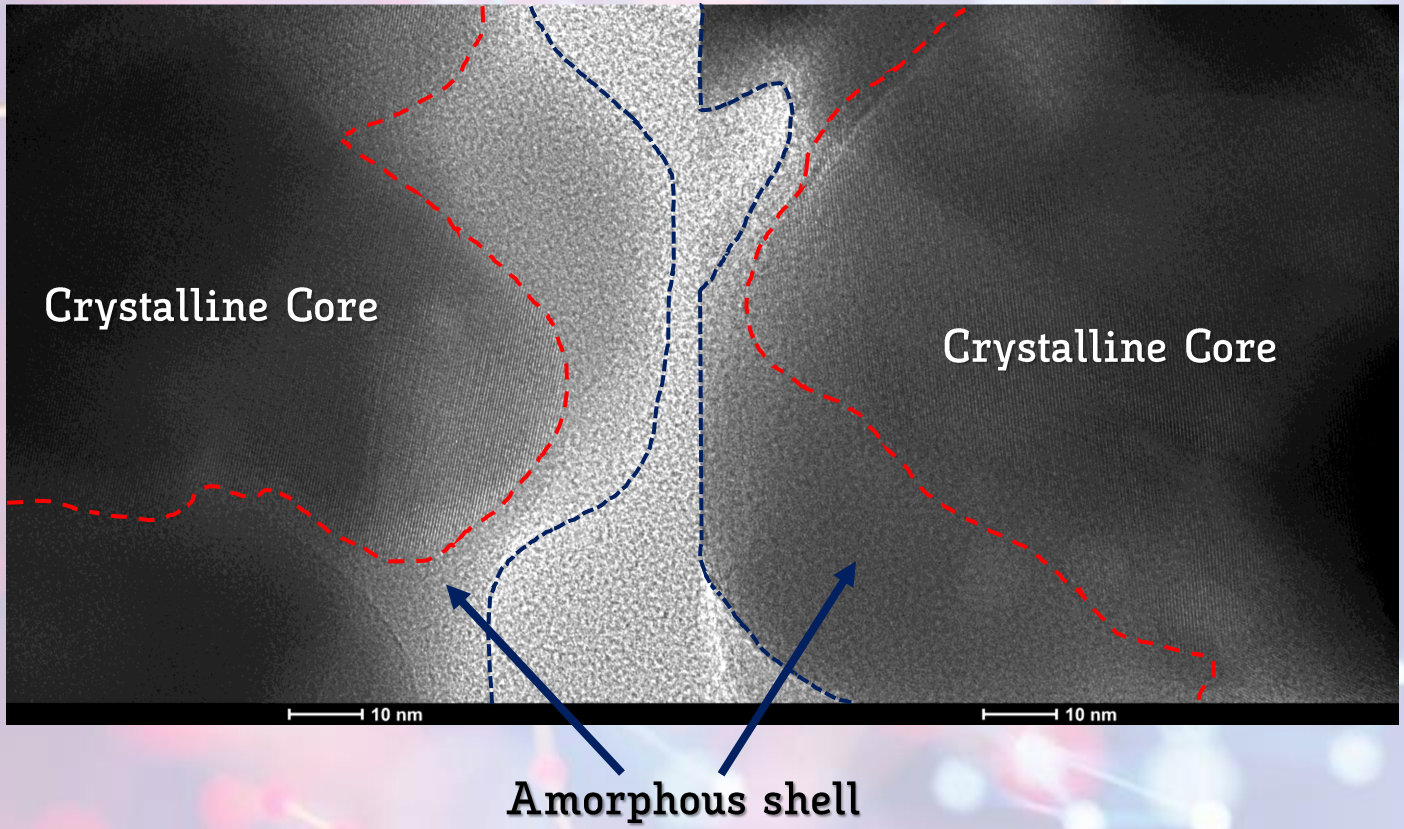

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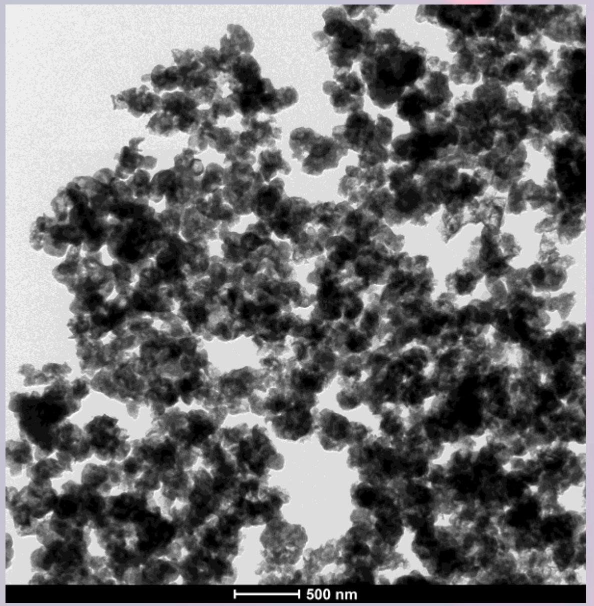

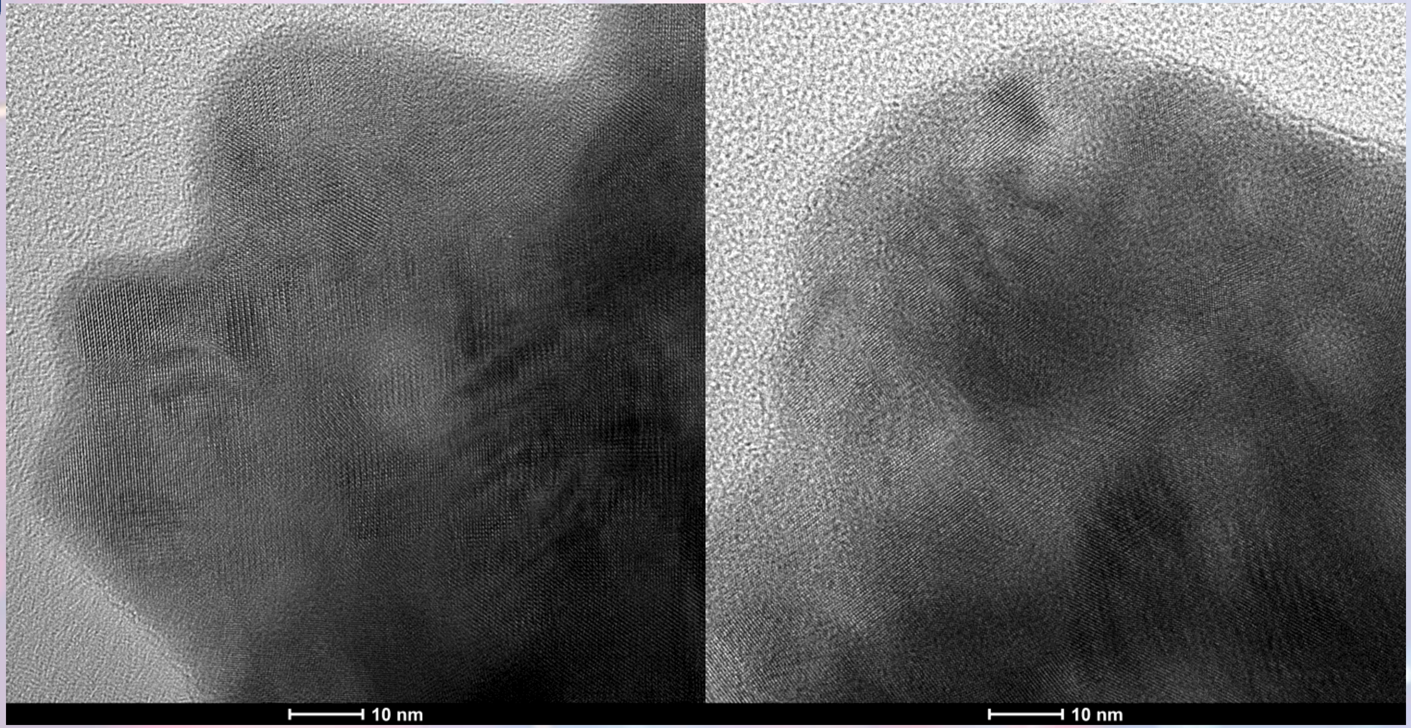

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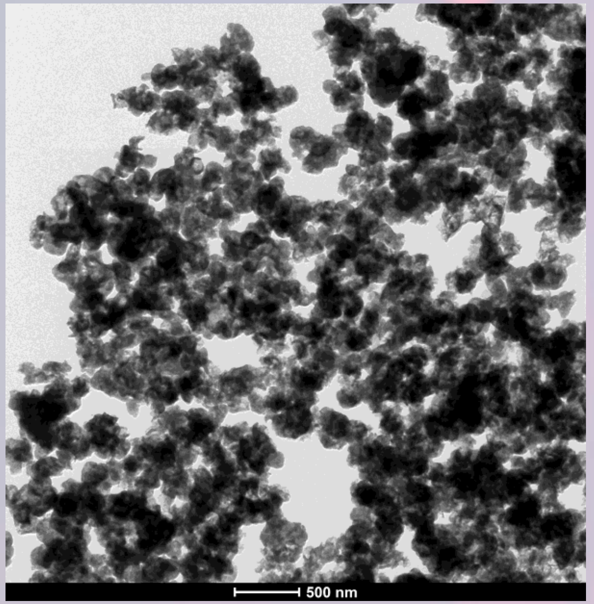

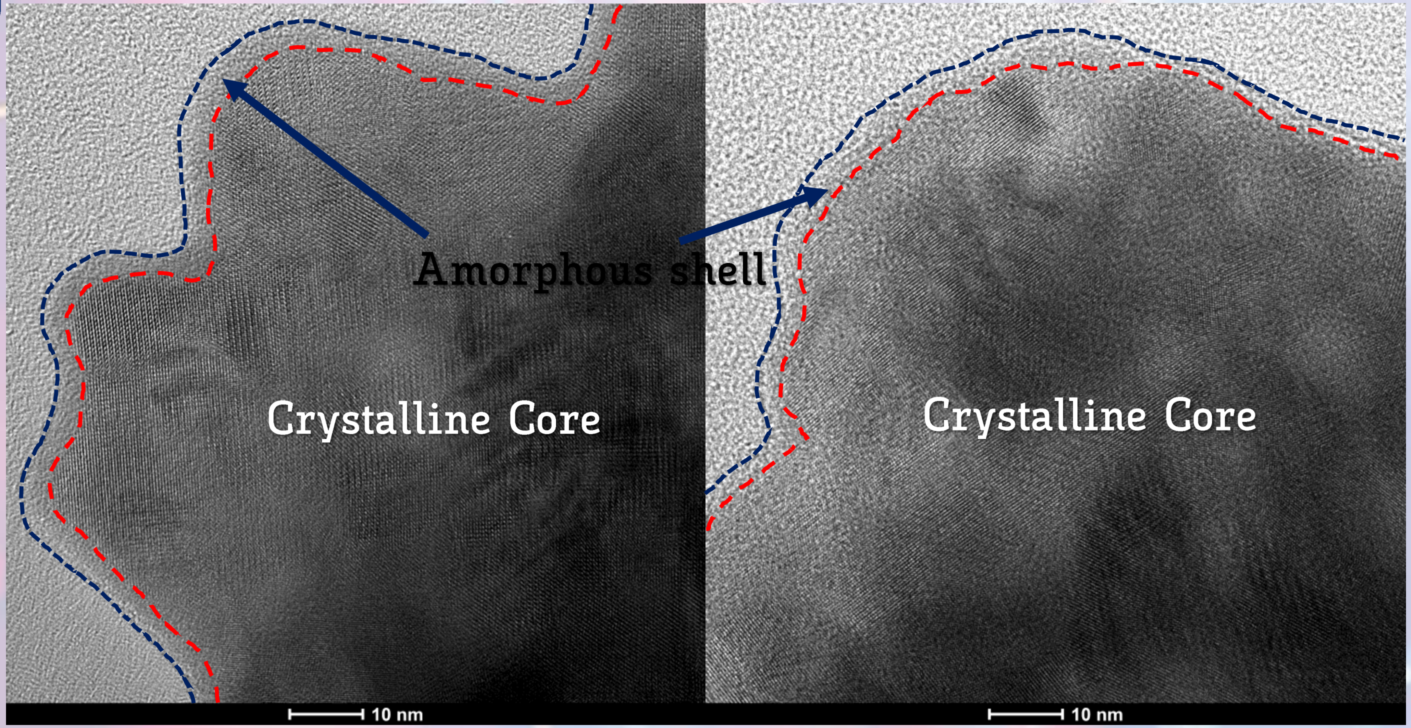

- By employing the ligand **N,N-bis(phosphonomethyl)glycinate**, a new family of **amorphous tin(IV) phosphonates** has been prepared, characterized and assayed as **precursors of tin(IV) pyrophosphate-based** proton conductors. Furthermore, the effect of incorporating **doping ions**, such as Al^{3+} and Mg^{2+}, has been investigated as possible way to **improve the proton conductivity properties**.

- The as-synthesized compounds exhibited **moderate proton conductivity** (~10^{-4} S·cm^{-1} at 90 °C, 95% RH). In contrast, by **pyrolyzing these compounds in air at 750 °C** the resulting tin(IV) pyrophosphates showed remarkably **higher proton conductivities**, up to ~10^{-2} S·cm^{-1} at 90 °C and 95% RH for $Sn_{0.8}Al_{0.2}$BPMGLY Δ750.

- Tin(IV) pyrophosphates so prepared were **fully characterized** by diverse solid-state techniques. In particular, the **MAS-NMR study** showed the presence of **hydrogen phosphate groups** in all samples after post-impedance measurements, which are apparently **responsible for the enhancement** of the proton conductivity.

- The tin(IV) pyrophosphates nanoparticles exhibited **a core-shell structural organization** as revealed by TEM.

- Further studies to evaluate the capabilities of these nanostructured compounds as proton conductors in **intermediate temperature fuel cells** (ITFC) are underway

ACKNOWLEDGMENTS:

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Prof. Enrique Ramírez Losilla

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