Sn(IV) Glyphosine Phosphonates as Precursor of Fast Proton Conductors based on SnP2O7

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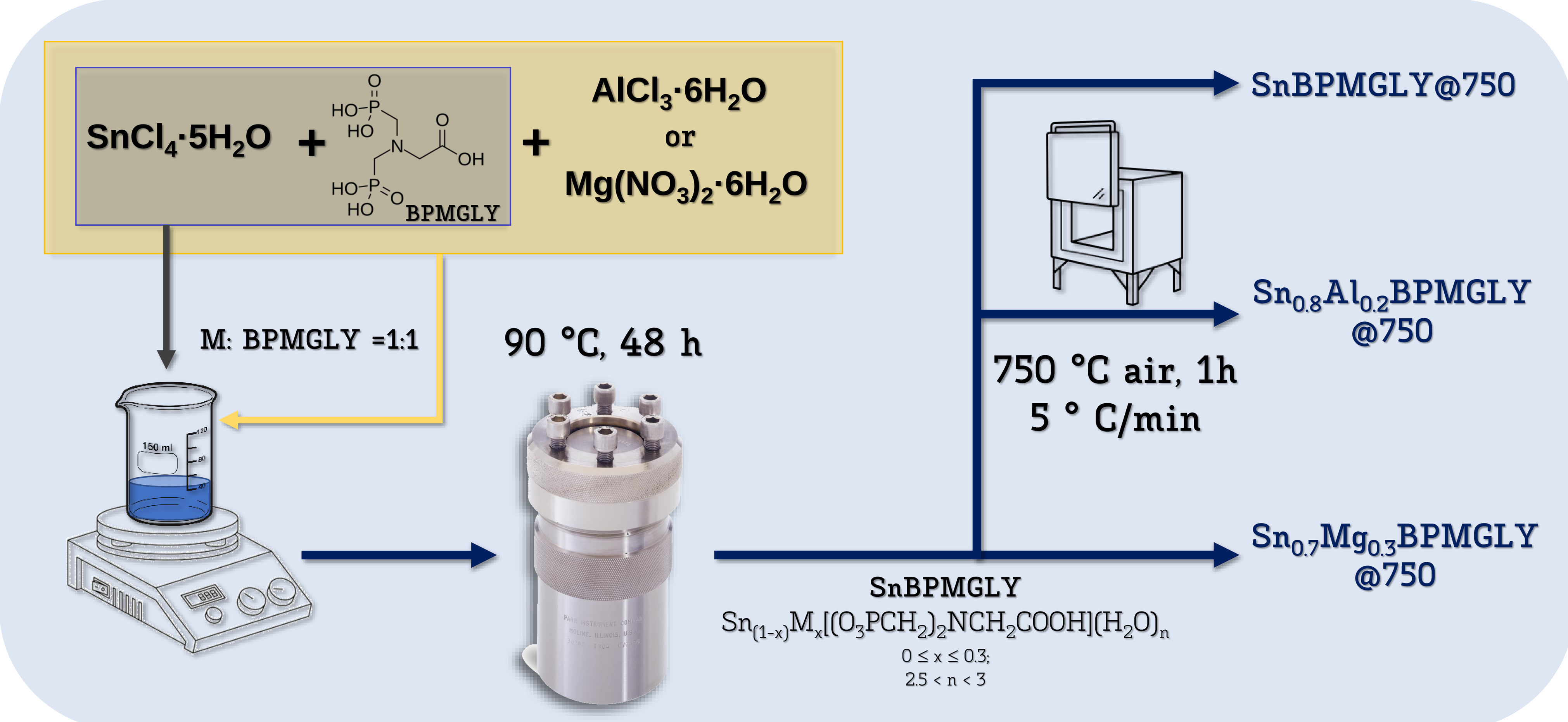
Introduction

Metal phosphonates (MPs) combine good chemical and thermal stability alongside tuneable properties, which provide appealing features for electrochemical applications [1-2]. They exhibit not only remarkable proton conductivity properties but also can be potential precursors of electrolytes. useable in intermediate-temperature fuel cells (ITFCs), operating at 100 - 250 ºC [3].

In this work, we report the synthesis and characterization of a **new family of amorphous tin(IV) glyphosine-based phosphonates**, $Sn_{1-x}M_x[(O_3PCH_2)_2–N–CH_2CH_2COOH]_{1-x}[(O_3PCH_2)_2–NH–CH_2CH_2COOH]_x·nH_2O$ (M = Mg^{2+}, Al^{3+}; x < 0.3).

Synthesis



Precursors characterization

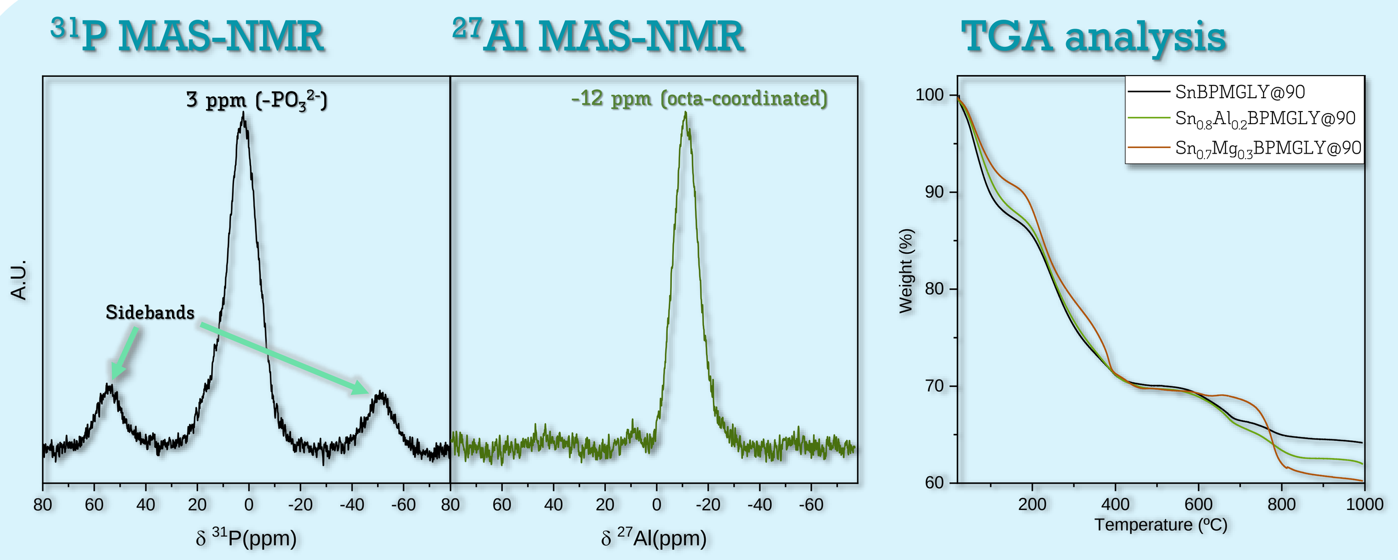
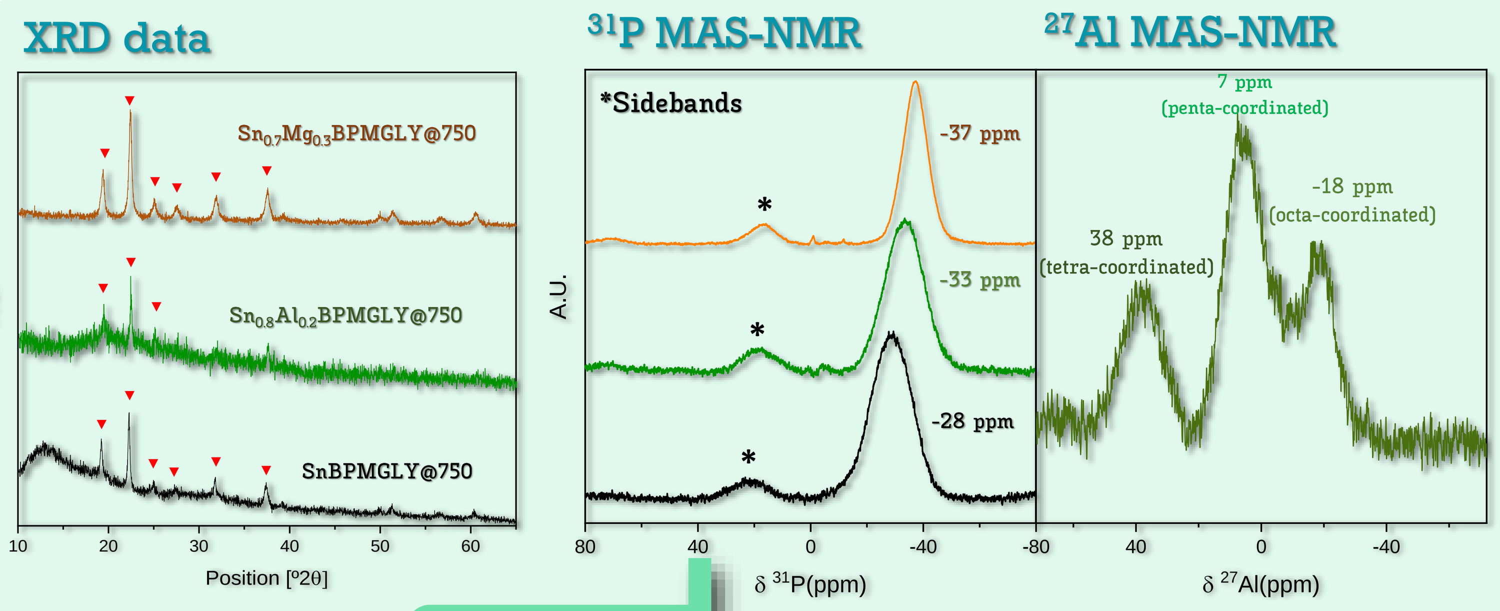


Figure 1. ^{31}P and ^{27}Al MAS-NMR spectra for undoped (black) and Al-doped (green) precursors (left) and TGA analysis of the three precursors (right).

Pyrophosphate derivatives characterization



90 °C
95 %RH

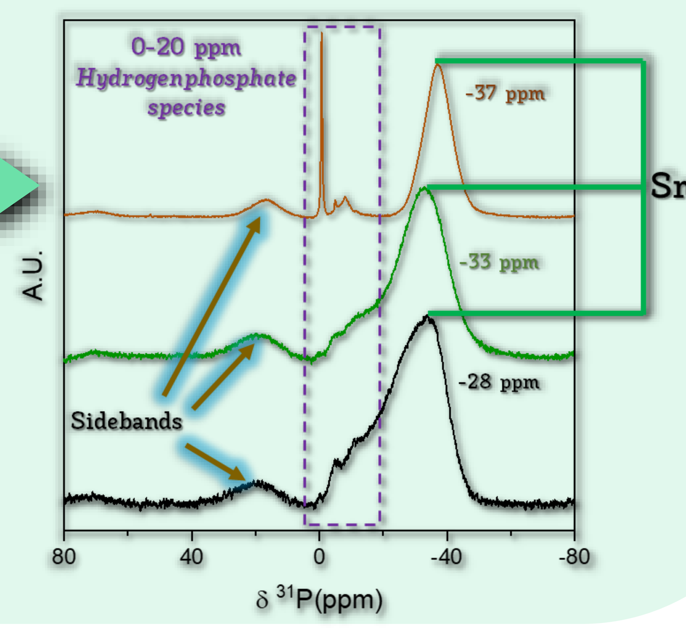


Figure 2. XRD patterns of the pyrophosphate derivatives showing the SnP_2O_7 (▼) phase (top left), and $^{31}P/^{27}Al$ MAS NMR spectra (top right). ^{31}P MAS NMR spectra after EIS measurements are shown at the bottom right.

TEM-EDS analysis

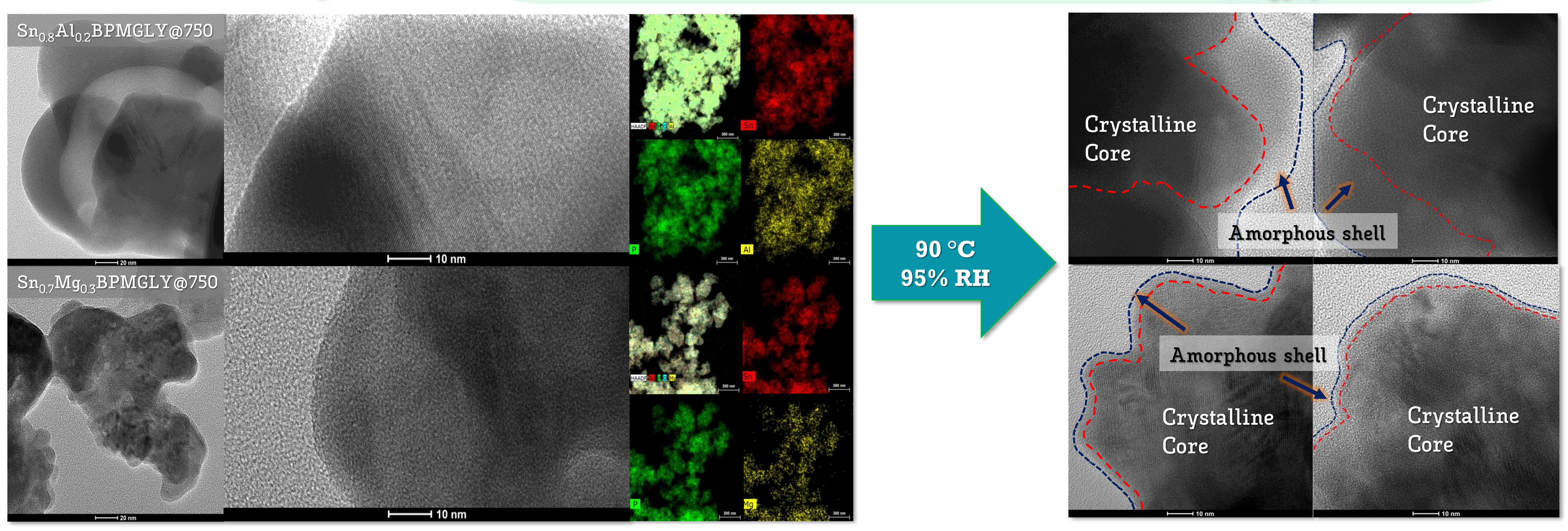


Figure 3. **TEM-EDS** analysis of both **doped pyrophosphate derivatives** as well as the study of the **core-shell** like structure of their particles after EIS measurements

Proton conductivity properties

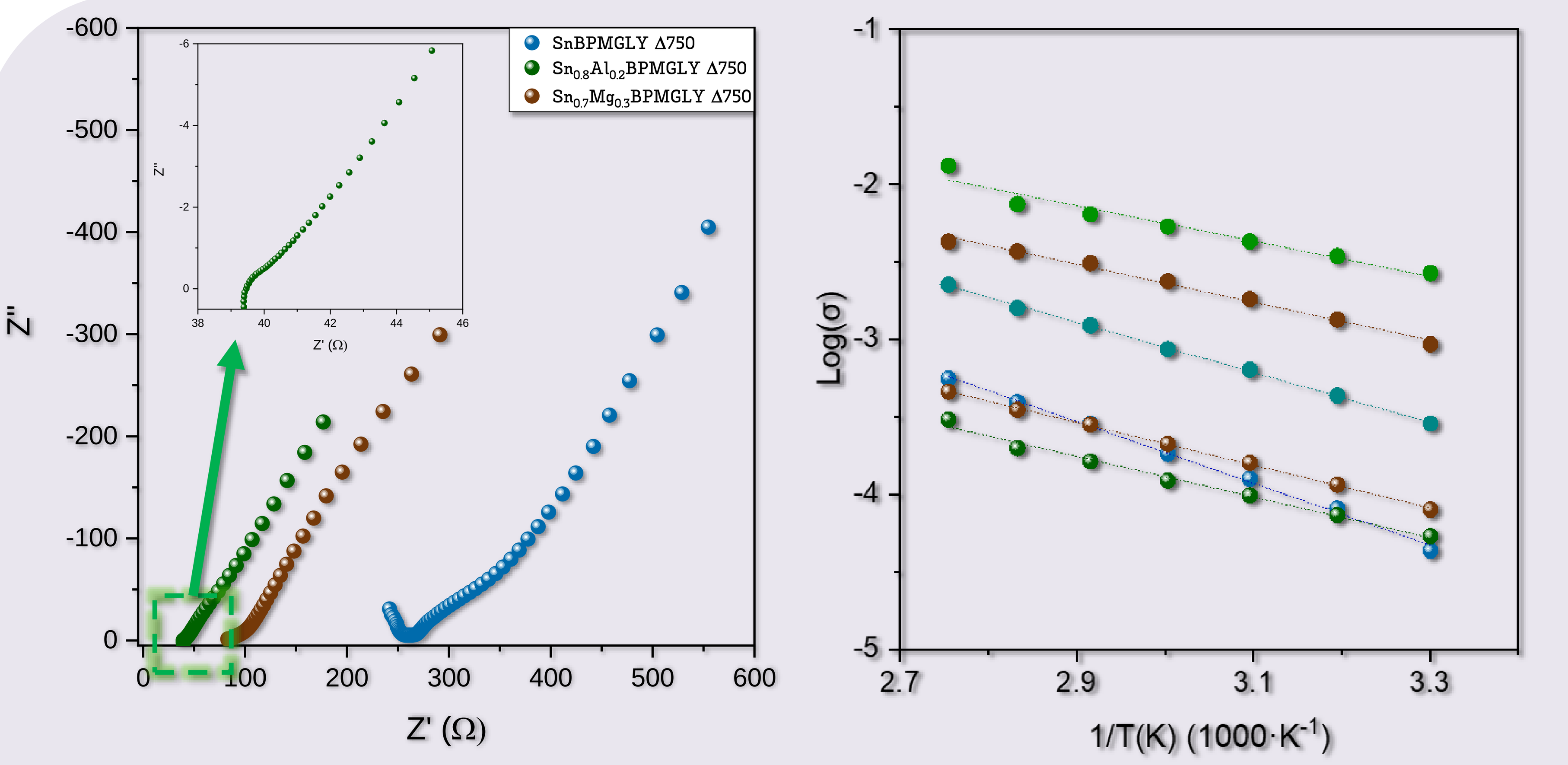


Figure 4. **Nyquist plots** of pyrophosphates derivatives (left) and **Arrhenius plots** of all samples.

Sample	σ (S·cm⁻¹)		Activation Energies (eV)
	90 °C, 95% RH	90 °C, 75% RH	95% RH
SnBPMGLY	$5.6 \cdot 10^{-4}$	$3.9 \cdot 10^{-5}$	0.326
$Sn_{0.8}Al_{0.2}BPMGLY$	$3.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	0.259
$Sn_{0.7}Mg_{0.3}BPMGLY$	$4.6 \cdot 10^{-4}$	-	0.243
SnBPMGLY@750	$2.2 \cdot 10^{-3}$	$4.8 \cdot 10^{-4}$	0.316
$Sn_{0.8}Al_{0.2}BPMGLY$ @750	$1.3 \cdot 10^{-2}$	$3.3 \cdot 10^{-3}$	0.226
$Sn_{0.7}Mg_{0.3}BPMGLY$ @750	$4.3 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	0.243

Table 1. **Proton conductivity** values of SnBPMGLY precursors and their pyrophosphate derivatives .

Conclusions

- A new family of amorphous tin(IV) phosphonates has been prepared, characterized and assayed as precursors of tin(IV) pyrophosphate-based proton conductors. The incorporation of doping ions (Al^{3+}/Mg^{2+}) has improved the proton conductivity up to **$1.3 \cdot 10^{-2}$ S·cm⁻¹** at 90 °C and 95% RH for **$Sn_{0.8}Al_{0.2}$BPMGLY@750**.
- 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.
- A **core-shell** structural organization of the materials' nanoparticles was revealed by **TEM**

Acknowledgments

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