

MS3 - O3: Proton Conductivity in Sulfate-Containing Lanthanide Nitrilotris-methylphosphonates

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Multifunctional metal phosphonates are coordination polymers (CPs) whose structures are usually composed of extended hydrogen-bond networks and thus making them potential candidates as proton conductors [1]. Moreover, these properties can be enhanced by appropriate modification of the synthesis conditions [2, 3].

In this communication, isostructural 2D layered compounds based on lanthanide nitrilotris-methylphosphonates are studied. In series 1 compounds, $\text{Ln}[(\text{ATMP})(\text{H}_2\text{O})_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Yb}^{3+}$), uncoordinated HSO_4^- acts as the counterion of positively charged layers creating an extended hydrogen-bond networks together with the lattice water molecules, while the lanthanide ions are octacoordinated by two water molecules and six oxygen from four different ligands. This phase transforms to other structures by dehydration or by exposing the samples at 80 °C and 95% relative humidity. Under wet conditions, the solids experience partial ($\text{Ln} = \text{Pr}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}$) or full loss ($\text{Ln} = \text{Yb}^{3+}$) of HSO_4^- , accompanied by a structural reorganization that influence the proton conductivity properties. In series 2, $\text{Ln}[(\text{ATMP})(\text{H}_2\text{O})](\text{SO}_4) \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$ and Tb^{3+}), the octacoordinated environment of lanthanide ions in the layer structure is composed of six phosphonate oxygen atoms and two oxygen from two sulfate ions which acts as a bridge ligands. This structural variability allows obtaining solids with conductivities ranging between $3.5 \cdot 10^{-2}$ and $1.0 \cdot 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ (80 °C and 95% RH) and activation energies corresponding to a Grotthuss-type proton transfer mechanism.