

PXRD and PDF analysis of multifunctional lanthanide nitrilotris-methylphosphonate-based proton conductors

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Metal phosphonates are multifunctional solids which possess tunable properties, such as H-bond networks, while exhibiting high chemical and thermal stability¹.

Depending on the protonation of the ligand, different crystalline phases can be obtained. Here, we report three different families of proton conductors based on lanthanide nitrilotris-methylphosphonates. Compounds having cationic layers compensate by chloride or sulfate anions were isolated: $[\text{Ln}(\text{H}_4\text{NMP})(\text{H}_2\text{O})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ ² and $\text{Ln}(\text{H}_5\text{NMP})\cdot\text{SO}_4\cdot 4\text{H}_2\text{O}$ [H_6NMP = nitrilotris(methylphosphonic acid)]. The crystal structure of $\text{Gd}(\text{H}_5\text{NMP})\cdot\text{SO}_4\cdot 4\text{H}_2\text{O}$ was solved ab initio from synchrotron powder diffraction data ($\lambda=0.4124$ Å, beamline BL04-MSPD ALBA) and refined by the Rietveld method. Chloride containing phases show two irreversible solid state transformations take place: (1) a crystalline-to-crystalline phase transition, $\{\text{Ln}-\text{H}_4\text{NMP} \rightarrow [\text{Ln}_2(\text{H}_3\text{NMP})_2(\text{H}_2\text{O})_4]\cdot 4.5\text{H}_2\text{O}$ for $\text{Ln}=\text{La}, \text{Pr}\}$, and (2) crystalline-to-amorphous phase transition, $\{\text{LnH}_4\text{NMP} \rightarrow [\text{Ln}(\text{H}_3\text{NMP})]\cdot 1.5\text{H}_2\text{O}$ for $\text{Ln}=\text{Gd}-\text{Ho}\}$, both implies the loss of HCl and structural rearrangements of the frameworks. Variations in average and local structure have been monitored by high resolution powder diffraction and PDF analysis, upon exposure the samples at high relative humidity and temperature (95% RH and 80 °C), in order to understand their behavior as proton conductors.

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