



Synthesis and Proton Conduction Properties of Lanthanide Amino-Sulfophosphonates

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Acidic groups-containing metal phosphonates exhibit a wide range of proton conductivity depending on the water content and functionality. Moreover, this property can be enhanced by appropriate post-synthesis chemical and/or thermal treatments [1,2].

In this work, focus is laid on properties derived from the combination of lanthanide ions with the amino-sulfophosphonate ligand $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{-N}(\text{CH}_2)_2\text{-SO}_3\text{H}$. Highthrough-put screening was used to reach the optimal synthesis conditions under hydrothermal conditions at 140 °C. Isolated polycrystalline solids, $\text{Ln}[(\text{O}_3\text{PCH}_2)_2\text{-NH}(\text{CH}_2)_2\text{-SO}_3\text{H}]\cdot 2\text{H}_2\text{O}$ (Ln= La, Pr, Sm, Eu, Gd, Tb and Er), crystallize in the monoclinic (La and Er) and orthorhombic (Pr, Sm, Eu, Gd and Tb) systems with unit cell volume of ~ 1200 and 2548 \AA^3 respectively. Their crystal structures, solved *ab initio* from X-ray powder diffraction data, correspond to different layered frameworks depending on the lanthanide cation size. Thus, compounds with orthorhombic symmetry show free acidic sulfonic pointing to the interlayer space, while La- and Er- derivatives display layered structures where both phosphonate and sulfonated groups are coordinated to the metal, leaving free P-OH groups. As consequence of this structural variability, different H-bond networks and proton transfer pathways are generated. Preliminary proton conductivity measurements have been carried out between 25 and 80 °C at 70-95 % relative humidity. The sample exhibits conductivities near to $3 \cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and activation energies characteristics of a Grotthuss-type mechanism of proton transfer.

Referencias

[1] Y. Gao, R. Broersen, W. Hageman, N. Yan, M.C. Mittelmeijer-Hazeleger, G. Rothenberg, S. Tanase, *J. Mater. Chem. A*, **2015**, 3, 22347-22352.

[2] A. Cabeza, P. Olivera-Pastor, R.M.P. Colodrero, *Tailored Organic-Inorganic Materials*, Brunet, E., Colón, J.L, Clearfield, A., Eds.; John Wiley & Sons, Inc. **2015**; Ch. 4, 137-191.