

Tunable crystal structure and proton conductivity of lanthanide nitrilotris-methylphosphonates.

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Metal phosphonates are multifunctional solids with remarkable stability and proton conducting properties owing to their structure is usually composed of extended hydrogen-bond networks that favor proton transfer pathways [1]. Moreover, these properties can be enhanced by appropriate modification of the synthesis conditions [2, 3].

In this communication, a new family of isostructural 2D layered compounds based on lanthanide nitrilotris-methylphosphonates is reported. These compounds have been isolated at room temperature and have the general formula $\text{Ln}[\text{N}(\text{CH}_2)_3(\text{PO}_3\text{H}_2)_2(\text{PO}_3\text{H})(\text{H}_2\text{O})]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (Ln= Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb). The coordination environment of Ln^{3+} is composed by eight oxygen atoms from three different ligands and two oxygens from bound waters. This connectivity creates positive charged layers connected to sulfate ions through hydrogen-bonds. These compounds show promising proton conductivity with values ranging between $7.6 \cdot 10^{-2}$ and $3.8 \cdot 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at 80 °C and 95% RH and low activation energy corresponding to Grotthuss-type proton transfer mechanism. In addition, a structural transformation occurs at $T > 70 \text{ °C}$ accompanied by a remarkable enhanced conductivity. Studies on the structure-properties relationships will be discussed.

References:

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