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 $Ln[N(CH_2)_3(PO_3H_2)_2(PO_3H)(H_2O)]SO_4 \cdot 2H_2O$ (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 $3.8 \cdot 10^{-2}$ $S \cdot cm^{-1}$ 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 °C accompanied by a remarkable enhanced conductivity. Studies on the structure-properties relationships will be discussed.

References:

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