

## Supplementary Information

### **Proton conduction in non-doped and acceptor-doped metal pyrophosphate (MP<sub>2</sub>O<sub>7</sub>) composite ceramics at intermediate temperatures**

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### $^{31}\text{P}$ MAS NMR spectra of non-doped and acceptor-doped $\text{MP}_2\text{O}_7\text{-MO}_2$

Figure S1 shows  $^{31}\text{P}$  MAS NMR spectra of non-doped and acceptor-doped  $\text{MP}_2\text{O}_7\text{-MO}_2$ . These spectra were measured at room temperature, where the chemical shift value was referenced to  $\text{H}_3\text{PO}_4$ . In the NMR spectra of  $\text{SnP}_2\text{O}_7\text{-SnO}_2$ ,  $\text{ZrP}_2\text{O}_7\text{-ZrO}_2$ , and Sm-doped  $\text{SnP}_2\text{O}_7\text{-SnO}_2$ , the peaks attributable to  $\text{MP}_2\text{O}_7$  appeared between -30 and -60 ppm, which means that the reaction between  $\text{MO}_2$  and  $\text{H}_3\text{PO}_4$  is based on the formation of chemical bonds. In contrast, in the NMR spectra of  $\text{TiP}_2\text{O}_7\text{-TiO}_2$  and  $\text{SiP}_2\text{O}_7\text{-SiO}_2$ , significantly large peaks ascribed to the orthophosphate group ( $\text{PO}_4^{3+}$ ) at approximately 0 ppm were observed in addition to the peaks assigned to  $\text{MP}_2\text{O}_7$ . It is thus confirmed that a part of  $\text{H}_3\text{PO}_4$  remains unreacted in the two samples.

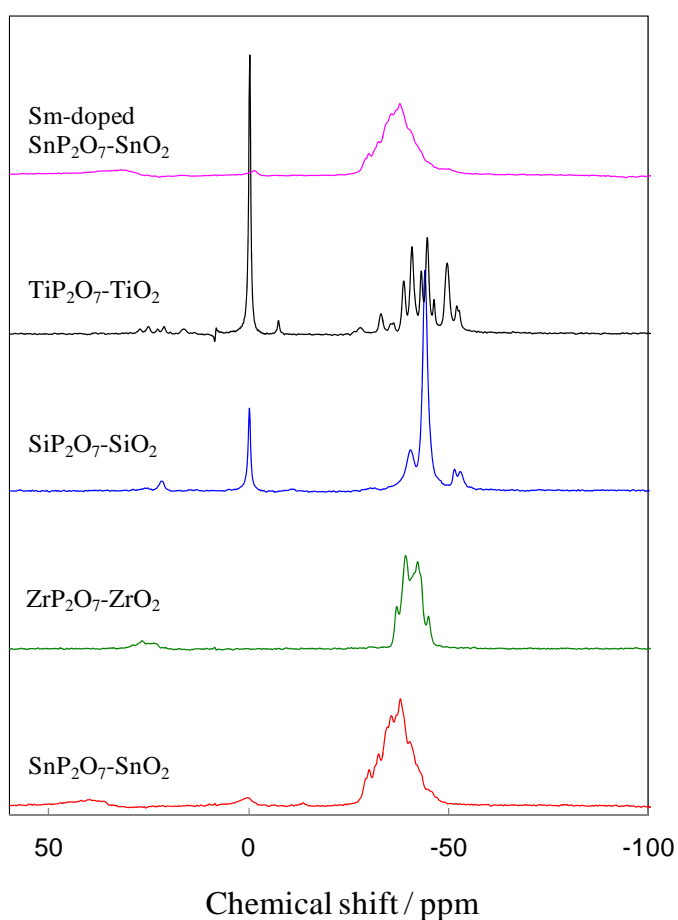


Figure S1

**Relationships between the electrical conductivity and the Sm<sup>3+</sup> content at various temperatures.**

Figure S2 shows that the proton conductivity monotonously increased with increasing Sm content, indicating that there is no percolation phenomenon for Sm<sup>3+</sup> dosage.

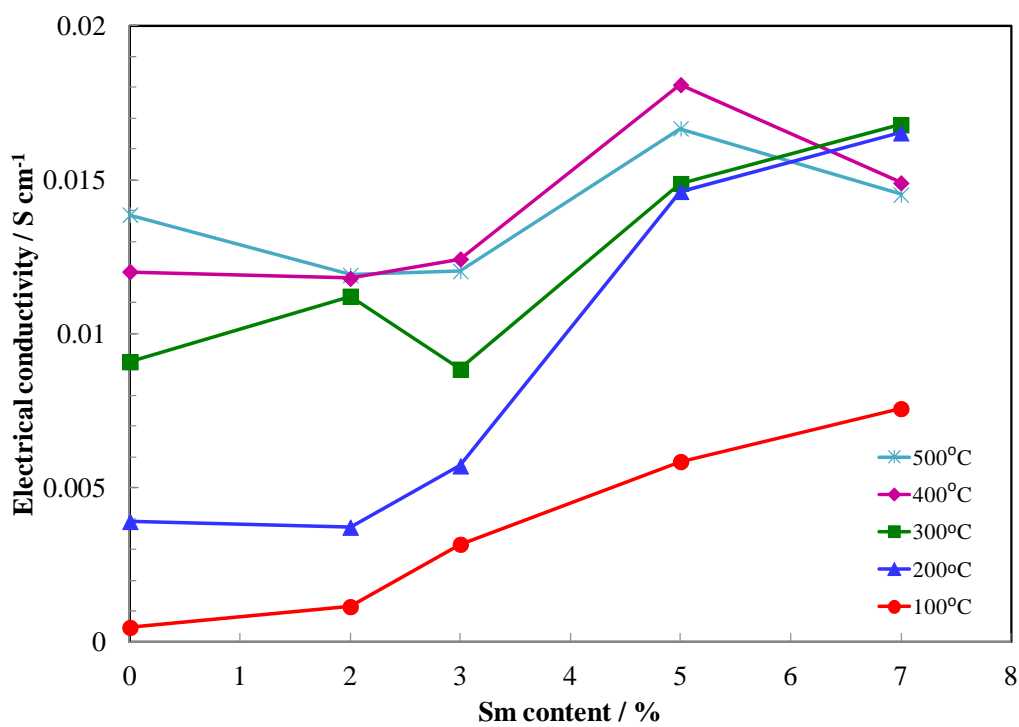


Figure S2