

Li⁺ and Al³⁺ site occupancies impact on ionic conductivity in Li_(7-3x)Al_xLa₃Zr₂O₁₂ garnet.

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Cubic garnets Li_(7-3x)Al_xLa₃Zr₂O₁₂ (LLAZO) exhibit high conductivity and are envisioned as electrolyte material for all-solid-state batteries. To better understand the role of Al³⁺, we investigated different Al-doped LLAZO prepared by conventional solid-state reaction. Cubic phase was formed at 900°C, confirmed by X-ray diffraction. Based on ⁶Li, ⁷Li and ²⁷Al MAS NMR spectroscopies, we identified for different Al doping levels the Li and Al site occupancies and investigated their mobility by ⁷Li static NMR with variable temperature. Ionic conductivity measurements on pellets were also performed using electrochemical impedance spectroscopy.

Li and Al site occupancies were found dependent on Al doping levels and strongly impact ionic mobility. From our measurements, garnet with x=0.35 exhibits higher ionic conductivity than with x=0.24. Al ions were mainly found at octahedral sites (96h) for x=0.35 whereas they were mainly on tetrahedral sites (24d) for x=0.24. More vacancies were also found on tetrahedral sites for x=0.35, that could facilitate [octa-tetra-octa] diffusion pathway. The latter have been shown to be more favorable energetically, i.e more mobility.

Some pellets were sintered using Spark Plasma Sintering (SPS) and further investigated. We found that SPS modifies the material as Li and Al site occupancies were different compared to non-sintered powders. Al occupancy on octahedral sites was increased for x=0.24 at levels comparable to non-sintered powders at x=0.35.