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ABSTRACT:

Compositional dependence of ionic conductivity in NaSICON materials from first principles

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NaSICON materials are a promising class of ion conductors for sodium ion solid state batteries. Particularly high conductivities are observed for compositions $Na_{1+x}M_2Si_xP_{3-x}O_{12}$ where the substitution of P^{5+} by Si^{4+} introduces additional mobile sodium ions. Despite the compositional flexibility of the structure, most studies focus on the highly conductive composition with Zr^{4+} on the *M*-sites. In the present study we investigate the impact of the type of *M*-cations and the variation of the substitution level x on the ionic conductivity in the rhombohedral NaSICON structure. The individual migration barriers on the atomic level are calculated by density functional theory and the macroscopic conductivity is simulated using subsequent kinetic Monte Carlo simulations.[1] On the one hand, we show that the interaction with Si^{4+} ions facilitates the migration of Na^+ ions leading to high conductivities at high substitution levels. On the other hand, the ionic conductivity depends on the size and electronic configuration of the *M*-cation. Moreover, the transport mechanism in the structure changes for specific M-cations and values of *x*.

[1] J. Schütt, F. Pescher, S. Neitzel-Grieshammer, Phys. Chem. Chem. Phys., 2022, 24, 22154.