Crystallography and crystal chemistry of NaSICONs

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Keywords: NaSICON, structure type, symmetry-adapted distortion modes.

A very large number of compositions $A_xM_2(TO_4)_3$ crystallize in the NaSICON crystal structure type built of corner-sharing octahedra $[MO_6]$ and tetrahedra $[TO_4]$. The voids in the framework can be either empty or filled with A cations (Figure 1). Such topology enables very rich crystal chemistry and remarkable flexibility, similar to that of the perovskite family. The NaSICON structure accommodates hundreds of M and T cation combinations, which leads to a wide range of physical properties. As a result, NaSICON-type materials find applications in very different areas, from nuclear waste immobilization to A-conducting solid electrolytes. Depending on composition and temperature, many NaSICONs also undergo displacive and order-disorder phase transitions.

The previous attempts to rationalize crystal chemistry of the NaSICON structure type had limited success, since the structure has eight internal degrees of freedom and thus no simple ‘tolerance factor’ could be established. In this talk, I will demonstrate that the R-3c structure with undistorted $[MO_6]$ octahedra and $[TO_4]$ tetrahedra can be used as a common reference point for any NaSICON-type material. More than 300 NaSICON-type oxides present in the Inorganic Crystal Structure Database were quantitatively analysed and it is shown that distortion from the ideal structure is primarily driven by the size mismatch between the A cations and $M_2(TO_4)_3$ framework, that can be used to optimize the geometry of the structure to control properties, such as A-ionic conductivity or thermal expansion. [1]

![Figure 1. General view of the $A_xM_2(TO_4)_3$ structure with M in $[MO_6]$ octahedra and T in $[TO_4]$ tetrahedra. The A1 and A2 labels indicate two inequivalent A sites with multiplicities 6 and 18, respectively](image)