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$In_2Ti_6(PO_4)_6[Si_2O(PO_4)_6]$ has been obtained by heating (1100 °C) stoichiometric amounts of In_2O_3, SiP_2O_7, TiP_2O_7, and TiO_2 in air. Colourless crystals of the phosphate-silicophosphate suitable for a single crystal structure investigation have been grown by chemical vapour transport (1000 °C → 900 °C, mixture of 70 mg $PtCl_2$ and 3.5 mg TiP as transport agent). $In_2Ti_6(PO_4)_6[Si_2O(PO_4)_6]$ adopts its own structure type ($R\bar{3}$ (No. 148), $Z = 3$, $a = 8.4380(10)$ Å, $c = 44.295(1)$ Å, 1809 independent reflections, 109 variables, $R1 = 0.044$, $wR2 = 0.112$).

The crystal structure represents a hybride built up from alternating layers (⊥ to the *c*-axis) of the NASICON structure-type and those showing the structure of silicophosphates $M_4[Si_2O(PO_4)_6]$. Isolated heteropolyanions $[Si_2O(PO_4)_6]^{12-}$ and double-octahedra $[In^{III}Ti^{IV}O_9]$ occur as coordination polyhedra besides isolated octahedra $[Ti^{IV}O_6]$ and tetrahedral phosphate groups. The results of ^{29}Si- and ^{31}P-MAS-NMR studies are in agreement with one crystallographically independent site for silicon and two sites for phosphorus. The phosphorus resonances can be related to the two sites by 2-dimensional cross-polarisation experiments, by the anisotropies of their chemical shifts, and by the observed line widths. All criteria lead to the same assignment. Substitution of In^{3+} by several trivalent transition metal ions leads to phosphate-silicophosphates $M_2Ti_6(PO_4)_6[Si_2O(PO_4)_6]$ ($M = Ti^{3+}$, V^{3+}, Cr^{3+}, Fe^{3+}).

Key words: Silicophosphate, NASICON, Crystal Structure, Chemical Vapour Transport, MAS-NMR