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The Origin of Phase Transition and the Usual Evolutions of the Unit-Cell Constants of the NASICON Structures of the Solid Solution $LiTi_{2-x}Ge_x(PO_4)_3$

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Ge-doped $LiTi_2(PO_4)_3$ has been synthesized by a conventional solid-state reaction. Compounds $LiM_2^{IV}(PO_4)_3$ with LTP-type structure present a different behaviour depending on nature of $M^{(IV)}$. For $M^{(IV)} = Ti$ and Ge, the structure shows the space group R3c, whereas for $M^{(IV)} = Ge$ the space group is R3. Differences in behaviour of $LiTi_2(PO_4)_3 - LiGe_2(PO_4)_3$ solid solutions are discussed in relation to the composition. Their structures $LiTi_{2-x}Ge_x(PO_4)_3$ $(0 \leq x < 2)$ were determined from X-ray powder diffraction method (XRD) using Rietveld analysis. A sharp change in the lattice parameter a is observed between the compositions with $x = 1$. The lattice parameter c increases as the Ge content increases in the whole range of composition. The space group R3c becomes R3 for the composition with $x > 1$. The SEM micrographs of the samples show relative porous microstructures due to the effect of the substitution.

Keywords: NASICON, origin of unusual evolutions of lattice parameters, phase transition, scanning electron microscopy SEM, X-ray diffraction DRX, Rietveld refinements