ANALYSIS OF THE NA-MN-TI-PO4 PHASE DIAGRAM USING FIRST-PRINCIPLES CALCULATIONS

Gustautas Snarskis[1], Linas Vilčiauskas[2]

[1]Faculty of Physics, Vilnius University, Vilnius, Lithuania
[2]Institute of Chemistry, Vilnius University, Saulėtekio al. 3, LT-10257 Vilnius, Lithuania
gustautass@gmail.com

The development of electrochemical rechargeable batteries is one of the current most important topics in science and technology. Although, lithium-ion batteries are becoming the leading technology, it faces a number of problems like safety and rare and expensive (cobalt, lithium) raw materials needed for production. Sodium-ion batteries are a viable alternative in applications where particularly high energy densities are not required and may be based on inexpensive and widespread materials [**?**]. Natrium SuperIonic Conductor (NASICON) framework compounds having the general formula of $Me'_xMe''_y(PO_4)_3$ (Me' = Na, Li, Me'' = Ti, V, Zr, Mn, Sc, Fe, etc.) are currently attracting massive attention from battery research community [**?**].

In this work a part of the Na-Mn-Ti-PO_4 phase diagram (Fig. **??**) corresponding to Mn solid solutions of different concentration in the NTP-123 system $Na_{(1+2x)}Mn_xTi_{(2-x)}(PO_4)_3$, where $x = 0.25; 0.5; 0.75; 1.0; 1.25; 1.5$, was constructed using periodic density function theory calculations and comparing the stability of these systems with the vertices of the ternary phase diagram taken as $NaTi_2(PO_4)_3$, Na_3PO_4 and $NaMnPO_4$. Calculations anticipate solid solutions to be stable at concentrations from $x = 0.5$ to $x = 1.5$, with $x = 1$ being the most stable, and $x = 0.5$ corresponding to the edge of the miscibility gap. The latter was shown to be stabilized by configurational entropy which was evaluated using a Cluster Expansion Approach together with Monte Carlo simulations [**?**].

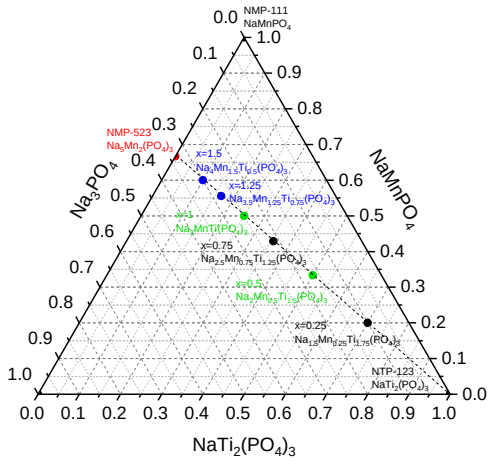

Fig. 1. Ternary phase diagram marked with calculated points corresponding to different concentrations.

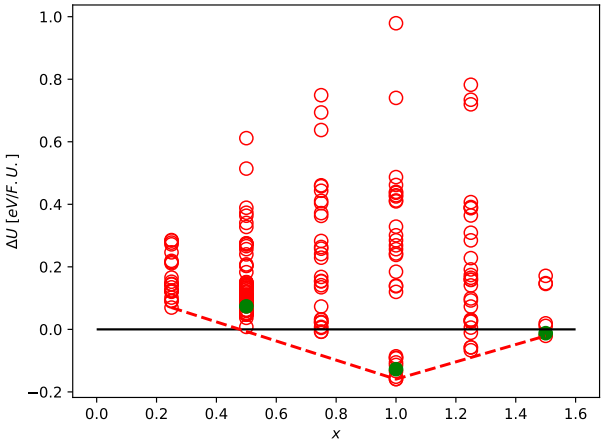

Fig. 2. Convex hull of $Na_{(1+2x)}Mn_xTi_{(2-x)}(PO_4)_3$. Red circles - PBE (GGA) formation energies, green dots - B1WC (Hybrid) formation energies.

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