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Anomalous Temperature Dependences of $\text{Na}_2\text{MnP}_2\text{O}_7$ Electrical Properties

S. Daugėla^{1*}, T. Šalkus¹, A. Kežionis¹, D. Valdniece², A. Dindune², M. Barre³,
A. F. Orliukas¹

- 1) Department of Radiophysics, Faculty of Physics, Vilnius University
2) Institute of Inorganic Chemistry, Riga Technical University
3) Institut des Molécules et Matériaux du Mans (IMMM, UMR 6283), Université du Maine, France

Saulėtekio ave. 9/3
LT-10222, Vilnius, Lithuania
Tel.: +370-5-2366064
saulius.daugela@ff.vu.lt

Abstract

$\text{Na}_2\text{MnP}_2\text{O}_7$ was proposed as a potential candidate for sodium-ion battery cathode [1]. Its structure and electrochemical properties were studied previously [2], however, all the investigations on this compound were only performed at room temperature. In the current work we study high temperature behavior of $\text{Na}_2\text{MnP}_2\text{O}_7$ powders and ceramics.

$\text{Na}_2\text{MnP}_2\text{O}_7$ was synthesized by solid state reaction. X-ray powder diffraction (XRPD) showed the triclinic symmetry of the compound (space group P1), identical to the one obtained in [2]. Differential thermal analysis clearly showed an endothermic peak at 670 K on heating the powder and an exothermic peak on cooling down. This suggested a structural phase transition of $\text{Na}_2\text{MnP}_2\text{O}_7$ and it was confirmed by thermal XRPD.

Impedance spectroscopy of the sintered $\text{Na}_2\text{MnP}_2\text{O}_7$ ceramics was performed in the frequency range of 10 Hz – 3 GHz and 300-700 K temperature interval. Surprisingly, a significant decrease of conductivity was observed up to 340 K. It was shown, that a very small amount of water in the sodium-manganese-pyrophosphates affects their room temperature conductivity, which must be mixed Na^+ and protonic at the same time. At 670-680 K, a sharp increase of conductivity and dielectric permittivity was associated with a phase transition taking place in $\text{Na}_2\text{MnP}_2\text{O}_7$. The anomalous change of electrical parameters at the phase transition temperature was frequency independent.

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[1] V. Palomares, et al., Energy Environ. Sci., 6 (2013) 2312.

[2] P. Barpanda, et al., Journal of Materials Chemistry A, 1 (2013) 4194.

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