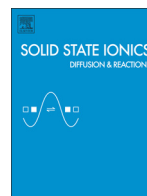




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Synthesis, structure and impedance spectroscopy of NaCsZn_{0.5}Mn_{0.5}P₂O₇ pyrophosphate ceramics

A.F. Orliukas^a, V. Venckutė^{a,*}, S. Daugėla^a, A. Kežionis^a, A. Dindune^b, D. Valdniece^b, J. Ronis^b, M. Lelis^c, M. Mosiałek^d, T. Šalkus^a

^a Faculty of Physics, Vilnius University, Saulėtekio 9/3, LT-10222 Vilnius, Lithuania

^b Institute of Inorganic Chemistry, Riga Technical University, Paula Valdena Str. 3/7, LV-1048 Riga, Latvia

^c Center for Hydrogen Energy Technologies, Lithuanian Energy Institute, Breslaujos St. 3, LT-44403 Kaunas, Lithuania

^d Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, PL-30239 Krakow, Poland

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ABSTRACT

NaCsZn_{0.5}Mn_{0.5}P₂O₇ powders were prepared by solid state reaction method. The study of the powder structure was conducted by X-ray diffraction (XRD) in temperature range from room temperature (RT) to 700 K. Rietveld analysis of XRD patterns showed that obtained NaCsZn_{0.5}Mn_{0.5}P₂O₇ is a mix of three phases: orthorhombic (s.g. *Cmc2*₁) NaCsMnP₂O₇, monoclinic (s.g. *P2*₁/*n*) NaCsZnP₂O₇ and monoclinic (s.g. *P2*₁/*n*) Cs₂MnP₄O₁₂. In the temperature ranges (400–500) K and (500–600) K the anomalies of lattice parameters for the NaCsMnP₂O₇ and Cs₂MnP₄O₁₂ phases respectively were found. The electrical properties of the sintered ceramics were investigated from RT to 700 K and in the frequency range 10–3 × 10⁹ Hz. The anomalies of electrical conductivity, dielectric permittivity and dielectric losses in investigated temperature ranges in these ceramics were found. This phenomenon can be associated with disordering in the lattices of NaCsMnP₂O₇ and Cs₂MnP₄O₁₂ compounds.

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1. Introduction

Li-ion batteries were prevailing over other batteries in the development of rechargeable batteries during last decades, because of their large energy density. However, the high cost and scarcity of lithium reserves has resulted in the pursuit of alternative energy-storage materials [1]. Recently, sodium ion batteries attract attention for use in energy-storage applications as cheaper alternative for lithium ion batteries. The limiting properties of cathode usually determine the electrochemical performance of the battery. A number of pyrophosphate compounds are known as attractive materials for cathodes of sodium ion batteries [2–10]. Currently, an abundant number of works addresses the synthesis conditions, structural and electrochemical characterizations of binary pyrophosphate compounds for rechargeable sodium-ion batteries. The most attractive pyrophosphates such as Na₂MnP₂O₇ [3], Na_{2–x}(Fe_{1–y}Mn_y)P₂O₇ (0 ≤ y ≤ 1) [3], NaFeP₂O₇ [5–8], polymorph β – Na₂MnP₂O₇ [8] crystallize in the triclinic structure (space group *P* $\bar{1}$), meanwhile NaCsMnP₂O₇ and Na₂CoP₂O₇ crystallize in the orthorhombic structure space group *Cmc2*₁ [3] and space group *Pna2*₁ [9] respectively. Na₂MnP₂O₇ exhibits good electrochemical activity at ~3.8 V (vs.

Na/Na⁺) with reversible specific capacity of 90 mAh/g at room temperature [10]. Galvanostatic charge/discharge measurements indicate that Na₂Fe_{0.5}Mn_{0.5}P₂O₇ is chemically active with a reversible capacity of ~80 mAh/g at a C/20 rate with an average redox potential of 3.2 V (vs. Na/Na⁺), showing promising cyclability and the rate capability is better than that of Na₂MnP₂O₇ [2]. The up-to-date results of investigations of pyrophosphates stimulate further research of pyrophosphate family and application of pyrophosphates as cathode materials for sodium ion secondary batteries. Application of pyrophosphate materials for batteries requires not only a good understanding of electrochemical properties, but also other characteristics. The aim of this work was to expand the knowledge about electrical properties of sodium containing pyrophosphates.

In the present work NaCsZn_{0.5}Mn_{0.5}P₂O₇ pyrophosphate powder was synthesized by solid state reaction and ceramics were sintered. The structure studies of the powder were conducted by X-ray diffraction (XRD) in the temperature range from room temperature (RT) to 700 K. The differential scanning calorimetry (DSC) and temperature gravimetric (TG) measurements were conducted from RT to 880 K. The chemical composition of the powder and ceramic samples were investigated with an attached energy dispersive X-ray spectrometer (SEM/EDX). The measurements of complex electrical conductivity ($\bar{\sigma} = \sigma' + i\sigma''$), complex impedance ($\bar{\rho} = \rho' - i\rho''$) and complex dielectric permittivity

* Corresponding author.

E-mail address: vilma.venckute@ff.vu.lt (V. Venckutė).

Table 1
Summary of X-ray diffraction analysis of NaCsZn_{0.5}Mn_{0.5}P₂O₇ powder at room temperature.

| Phase | Space group | a, Å | b, Å | c, Å | β | V, Å ³ | Z | d _t , g/cm ³ |
|--|--------------------|------------|------------|------------|------------|-------------------|---|------------------------------------|
| NaCsMnP ₂ O ₇ | Cmc2 ₁ | 5.3203(4) | 15.0477(5) | 7.9974(3) | | 784.370 | 4 | 3.534 |
| NaCsZnP ₂ O ₇ | P2 ₁ /n | 13.0105(2) | 7.6912(6) | 7.4241(5) | 91.030(2) | 742.797 | 4 | 3.259 |
| Cs ₂ MnP ₄ O ₁₂ | P2 ₁ /n | 7.9809(2) | 13.2416(2) | 11.5396(2) | 101.988(3) | 1192.912 | 4 | 3.545 |

($\bar{\epsilon} = \epsilon' - \epsilon''$) of the ceramics were carried out in air in the temperature interval from RT to 700 K and in the frequency range from 10 Hz to 3 GHz.

2. Experimental

NaCsZn_{0.5}Mn_{0.5}P₂O₇ powders were prepared by a solid-state reaction method from stoichiometric mixture Na₂CO₃, ZnO, MnO, CsNO₃ (all precursors were chemically pure) in Ar/H₂ atmosphere. The stoichiometric mixture was mixed and 85% H₃PO₄ solution (diluted with distilled water 1:1) was added very slowly and the mixture was mixed again. The obtained product was heated in silica-carbon crucibles in Ar/H₂ atmosphere at temperature 393 K for 4 h. After milling the obtained powder was pressed into pellets at 50 MPa. The pellets were sintered at temperature 673 K for 6 h and then they were sintered at temperature 923 K for 4 h. Tubular furnace was used for sintering under steady Ar/H₂ flow. After annealing the obtained product in Ar/H₂ atmosphere it was cooled down to RT. The obtained product was milled into powder again and powder was heated at temperature 993 K for 4 h.

Bruker D8 X-ray diffractometer equipped with MRI Physikalische Geräte GmbH TC-BASIC heating chamber was used to measure XRD patterns of the synthesized powders at room and elevated temperatures. XRD patterns were investigated using CuKα radiation in the 2θ region of 10–60 degrees with step size of 0.01 degree. XRD patterns during heating and cooling were recorded with a 20 K temperature step. While changing between two temperature levels heating and cooling rate was 10 degrees per minute. In order to achieve thermal equilibrium and completeness of the processes after reaching each temperature level, sample was kept at a selected temperature for 60 or 20 min during heating and cooling processes respectively. Scan rate for pattern recording during heating was roughly 0.175 degree per minute, during cooling – 0.25 degree per minute, at RT and 700 K temperature – 0.1 degree per minute. Analysis of the measured data was done by TOPAS v.4.1 software.

The differential scanning calorimetry and temperature gravimetric measurements were conducted with Netzsch STA 409 PC Luxx setup in Ar gas (99.999%) (Linde Gaz Polska). The flow rate of argon was 60 cm³·min⁻¹.

The ceramic samples for electrical properties measurements were sintered. The powders were uniaxially pressed into pellets at 250 MPa. NaCsZn_{0.5}Mn_{0.5}P₂O₇ pellets were sintered at temperature 953 K for 2 h in air. The densities of the ceramics were calculated from geometrical and weight measurements and found to be 3.08 g/cm³. SEM/EDX (TM3000 – Hitachi) was used for analysis of chemical composition of investigated ceramic samples and powder. The chemical composition of ceramics and SEM images were obtained after measurements of electrical properties of the samples. The measurements of electrical properties of NaCsZn_{0.5}Mn_{0.5}P₂O₇ ceramic samples in the low frequency range (10 Hz–2 MHz) were carried out by the two probe method [11]. The electrodes were fired at 920 K on the sintered cylindrical samples by applying conductive Pt paste (Gwent Electronics Materials Ltd.). The measurements in the microwave range (3 × 10⁵–3 × 10⁹) Hz were performed by Agilent Network Analyzer E5062A connected to the coaxial line, the part of inner conductor of coaxial line was replaced by the sample. The impedance of the sample was calculated from scattering parameters of such network as in [12]. The temperature measurements of the ceramics in the low and high frequency ranges were performed in

the range 300–700 K using Digital Thermometer TMD90A. The temperature was controlled by a computer connected to a dc power supply.

3. Results and discussion

The results of XRD measurements show that NaCsZn_{0.5}Mn_{0.5}P₂O₇ powder prepared by solid state reaction are mixed phase compound. Three different phases were detected in the X-ray diffraction patterns of the powder. NaCsZnP₂O₇ (65.61 wt.%), NaCsMnP₂O₇ (15.35 wt.%) and Cs₂MnP₄O₁₂ (19.04 wt.%) phases were found in the powder at room temperature. We haven't found the information about structure measurements of NaCsZnP₂O₇ compound in the literature. The results of analysis of XRD patterns show that NaCsZnP₂O₇ compound belongs to monoclinic symmetry (space group P2₁/n) with four formula units in the unit cell. The analysis of NaCsMnP₂O₇ XRD patterns show that this phase crystallizes in the orthorhombic symmetry (space group Cmc2₁) (No. 36 card 089-5449) and this result is in good correlation with [3]. The Cs₂MnP₄O₁₂ crystallizes in monoclinic structure (space group P2₁/n) as it was reported in [13]. The lattice parameters, unit cell volume (V), angle (β), formula units in the unit cell (Z) and theoretical density (d_t) of the three phases at RT are presented in Table 1.

Pseudo 3D montage of XRD patterns of NaCsZn_{0.5}Mn_{0.5}P₂O₇ powder is recorded during in-situ heating and cooling in 300–700 K temperature range.

XRD patterns recorded during heating and cooling processes do not reveal any appearance or disappearance of the peaks (Fig. 1). As the only certain difference between patterns at different temperatures is continuous shift of the peaks towards lower 2θ values during heating and towards higher 2θ values during cooling, it is presumed that there are no changes in the phase composition of the sample and all changes are related to the lattice parameter variation due to the thermal expansion.

The temperature dependences of the lattice parameters of the NaCsMnP₂O₇, NaCsZnP₂O₇ and Cs₂MnP₄O₁₂ compounds at heating and cooling are presented in Fig. 2a, b and c respectively. In the temperature region (400–500) K the anomalies of lattice parameters and cell volume in the NaCsMnP₂O₇ XRD patterns were found. The anomalies of a, b, c and V lattice parameters in the Cs₂MnP₄O₁₂ phase are detected in the temperature range (500–600) K. These anomalies remain in NaCsMnP₂O₇ and Cs₂MnP₄O₁₂ phases at cooling of the powder to room temperature. The temperature hysteresis of b, c and V lattice

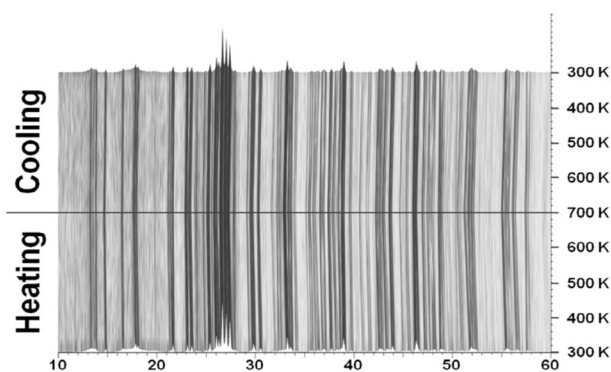


Fig. 1. Pseudo 3D montage of XRD patterns of NaCsZn_{0.5}Mn_{0.5}P₂O₇ powder at heating and cooling in 300–700 K temperature range.

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