Poster Presentations

[MS28-P01] The crystal structure of Li3(V,P)O4 – a novel potential phase for electrochemical applications

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Lithium vanadate, Li_3VO_4 is isostructural to Li_3PO_4 – an advanced material for rechargeable lithium-ion batteries. Li_3VO_4 and Li_3PO_4 are known to have several polymorphs: the β_{II}-forms (sp. gr. $Pmn2_1$) are stable in low temperature and the γ-forms (sp. gr. *Pmnb*) are generally stable in high temperature. Lithium vanadate shows high conductivity in the γ-form because of the lithium-ion mobility in the structure [1]; relatively high room temperature conductivity is reported for the β_{II}-form [2]. Furthermore, the β_{II}-form has attractive properties for optic materials: it was found that β_{II}-Li_3VO_4 shows second harmonic generation activity [3]. The crystal structures of both polymorphs are built up of oxygen atoms in the hexagonal close packing oriented perpendicular to the *c* axes. The Li^+ and V^{5+}/P^{5+} cations occupy half of the tetrahedral voides. The non-centrosymmetric β_{II}-form consists of only corner-sharing tetrahedra. The γ-form is built up by both corner and edge sharing tetrahedra. In the Li_3PO_4 structure *a*/*c* unit cell parameters of the two different polymorphs are almost the same – 6.115(1)/4.8554(1) and 6.120(2)/4.9266(7) Å, for β_{II}-and γ-form, respectively; whereas the *b* parameter of β_{II}-form, 5.2394(11) Å, is doubled in the γ-form and [4][6][4] equal to 10.490(3) Å. Numerous synthetic compounds with the general formula $^{[4]}Li_x\ ^{[6]}M\ ^{[4]}TO_4$ (*M* = Fe, Mn, Co, Ni, Zn; *T* = P, V, As, Si, Ge) are closely related to Li_3PO_4. Such compounds show similar physical properties and form solid solutions between the end members. Moreover, γ-Li_3PO_4 occurs in nature as the mineral lithiophosphate; its Na-species is known as the mineral nalipoite $NaLi_2PO_4$.

Translucent pale yellow crystals of $Li_3(V,P)O_4$ with prismatic shape were formed by hydrothermal synthesis. A mixture of Li_3PO_4, Li_2CO_3, V_2O_5, and H_2O in a weight ratio of 1 : 1 : 1 : 5 was placed in a 4 ml PTFE-lined stainless steel autoclave. The reaction time at $T = 280^{\circ}C$ and P = 70 bar was 18 days. The presence of V, P, and O in the samples was confirmed by qualitative X-ray elemental microanalysis.

The $Li_3(V_{0.7}P_{0.3})O_4$ crystal structure was determined by single crystal X-ray diffraction: a = 6.3050(12), b = 10.921(2), c = 4.9450(10) Å, $Pbn2_1$, Z = 4, ρc = 2.799 g/cm^{-3}, $R1$ = 0.0279, $\omega R2$ = 0.0432. The crystal chemical similarity of the discussed compounds allow us to consider the $Li_3(V,P)O_4$ as a perspective material for electrochemical applications. Note that in the $^{[4]}Li_x\ ^{[6]}M\ ^{[4]}TO_4$ -family, $Pbn2_1$ space group is known only for the Li_2CoSiO_4, which also crystallizes in $Pmn2_1$ and *Pmnb* space groups [4].

[1] Rodger A. R., Kuwano J., West A. R. (1985). Solid State Ion. **15**, 185-198.
[2] Song X., Jia M., Chen R. (2002). J. Mater. Process. Technol. **120**, 21-25.
[3] Sakata S., Fujii I. (1991). Jpn. J. Appl. Phys. **30**, L1489-L1492.
[4] M.E. Arroyo y de Dompablo, U. Amador, et al. (2009). J. Power Sources. **189**, 638-642.

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