$Li_{1+y}Ti_{2-x-y}Ge_xAl_y(PO_4)_3$ NASICON-type electrolytes with enhanced conductivity for solid state lithium-ion batteries

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The use of NASICON-type phosphates in lithium-ion batteries

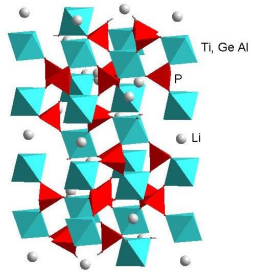
advantages:
- ✓ More resistant to high temperatures,
- ✓ Less flammable
- ✓ More electrochemically stable

disadvantages:
- ✓ Low ionic conductivity
- ✓ Poor contact of the electrode and electrolyte

Lithium-titanium phosphates - $LiTi_2(PO_4)_3$
Space group R-3c; a= 8,5129 Å, c = 20,8780 Å
Ionic conductivity $\sigma < 10^{-6}$ S/cm at 50°C

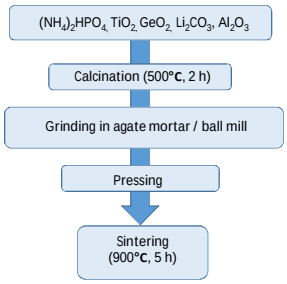
Enhancing ionic conductivity:
Iso- and heterovalent doping

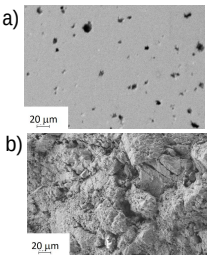
The aim of this research:
Synthesis and investigation of ionic conductivity $Li_{1+y}Ti_{2-x-y}Ge_xAl_y(PO_4)_3$(y = 0-0.3)



Crystal structure of $Li_{1+y}Ti_{1.6}Ge_{0.2}Al_{0.2}(PO_4)_3$

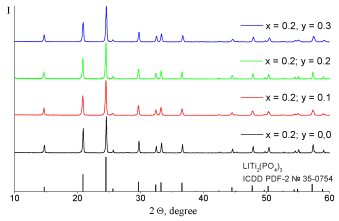
Synthesis scheme



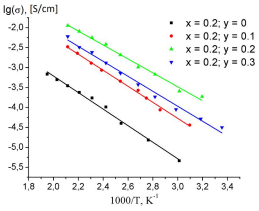


SEM-images of polished pellets of $Li_{1+y}Ti_{1.6}Ge_{0.2}Al_{0.2}(PO_4)_3$ prepared with different modes of precursor ball-milling: a) 400 rpm, 99 cycles; b) 600 rpm, 99 cycles

Influence of heterovalent doping of $LiTi_2(PO_4)_3$ on ionic conductivity



XRD patterns of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$*



Variation of log(σ) vs 1000/T for $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$

Unit cell parameters of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$ (space group R-3c)

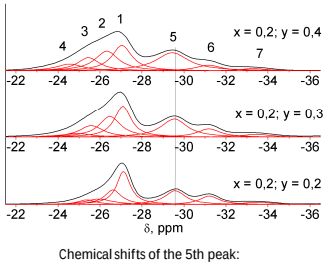
y	a, Å	c, Å
0	8,4924(5)	20,851(4)
0.1	8.4774(4)	20.876(2)
0.2	8.4752(8)	20.880(5)
0.3	8.4594(4)	20.833(2)

Activation energy of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$

y	E_a, kJ/mol
0	40 ± 1
0.1	38 ± 1
0.2	31 ± 1
0.3	36 ± 1

* The highest ionic conductivity of $LiTi_{2-x}Ge_x(PO_4)_3$ was found for x = 0.2 / *Kurzina E. A., Stenina I. A., Dalvi A., Yaroslavtsev A.B.* Synthesis and Ionic Conductivity of Lithium Titanium Phosphate-Based Solid Electrolytes. *Inorg. Mater.* 57 (2021) 1035–1042

^{31}P MAS NMR of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$

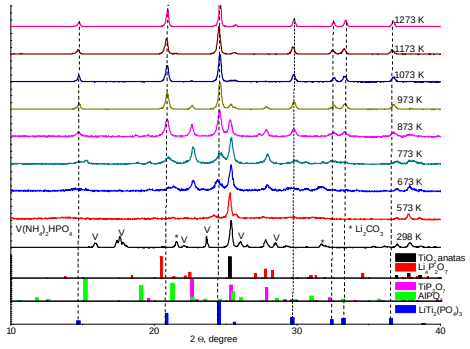


Chemical shifts of the 5th peak:

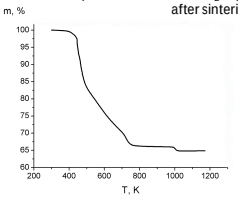
X = 0,2; y = 0,2 δ = - 29,57 ppm
X = 0,2; y = 0,3 δ = - 29,53 ppm
X = 0,2; y = 0,4 δ = - 29,45 ppm

	Environment	Peak area, %		
	X = 0,2	Y=0,2	Y = 0,3	Y= 0,4
1	PO_4Ti_4	31,04	24,54	22,59
2	PO_4Ti_3Al	16,92	22,36	20,63
3	$PO_4Ti_2Al_2$	6,93	9,08	13,07
4	PO_4TiAl_3	8,96	8,87	8,12
5	PO_4Ti_3Ge + PO_4Ti_2GeAl	19,50	21,43	26,08
6	$PO_4Ti_2Ge_2$	11,46	8,00	6,40
7	PO_4TiGe_3	4,12	4,07	2,91

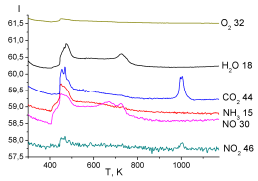
Investigation of sintering process of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$



XRD patterns of a mixture Li_2CO_3+3.2TiO_2+0.4GeO_2+0.2Al_2O_3+6$(NH_4)_2HPO_4$ at 298 K and after sintering for 5 h at different temperatures

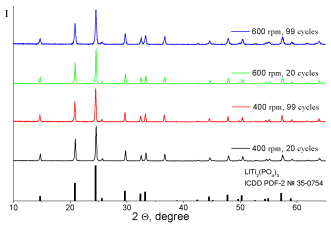


Weight loss curve of a mixture Li_2CO_3+3.2TiO_2+0.4GeO_2+0.2Al_2O_3+6$(NH_4)_2HPO_4$

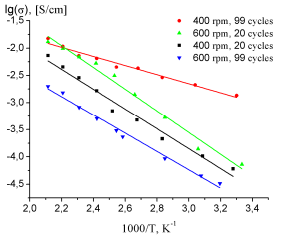


Ion currents at thermal analysis of a mixture Li_2CO_3+3.2TiO_2+0.4GeO_2+0.2Al_2O_3+6$(NH_4)_2HPO_4$

Influence of precursor ball-milling on ionic conductivity of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$



XRD patterns of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$ prepared with different modes of precursor ball-milling



Plots of log(s) vs 1000/T for $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$ prepared with different modes of precursor ball-milling

Influence different machining on parameters of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$

Rate of ball milling, rpm	Number of cycles	Pellet density, %	Conductivity (298 K), S/cm	E_a, kJ/mol
400	20	85	$6{,}6\cdot10^{-5}$	35 ± 2
400	99	97	$1{,}4\cdot10^{-3}$	16 ± 2
600	20	88	$7{,}3\cdot10^{-5}$	38 ± 2
600	99	73	$3{,}3\cdot10^{-5}$	32 ± 1

Conclusions:

✓$Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$ compounds were prepared by solid state reaction and characterized by X-ray diffraction, scanning electron microscopy, ^{31}P MAS NMR and impedance spectroscopy.

✓The optimal germanium content has been determined. The aluminum doping results in increase in lithium conductivity.

✓$Li_{1.2}Ti_{1.6}Ge_{0.2}Al_{0.2}(PO_4)_3$ exhibits the highest ionic conductivity at room temperature ($1{,}4\cdot10^{-4}$ S/cm).

✓Detected ^{31}P NMR signals have been assigned to different $PO_4Ti_{4-n-m}Ge_nAl_m$ arrangements assuming a random distribution of Ti,Al, and Ge cations in NASICON compounds. The intensity of the components located at less negative values becomes more intense as the Al content increases.

✓The formation of $Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO_4)_3$ occurs through the intermediate formation of titanium pyrophosphate.

✓The precursor ball-milling before the final annealing leads to a conductivity increase.