

Li_{1+y}Ti_{2-x-y}Ge_xAl_y(PO₄)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:

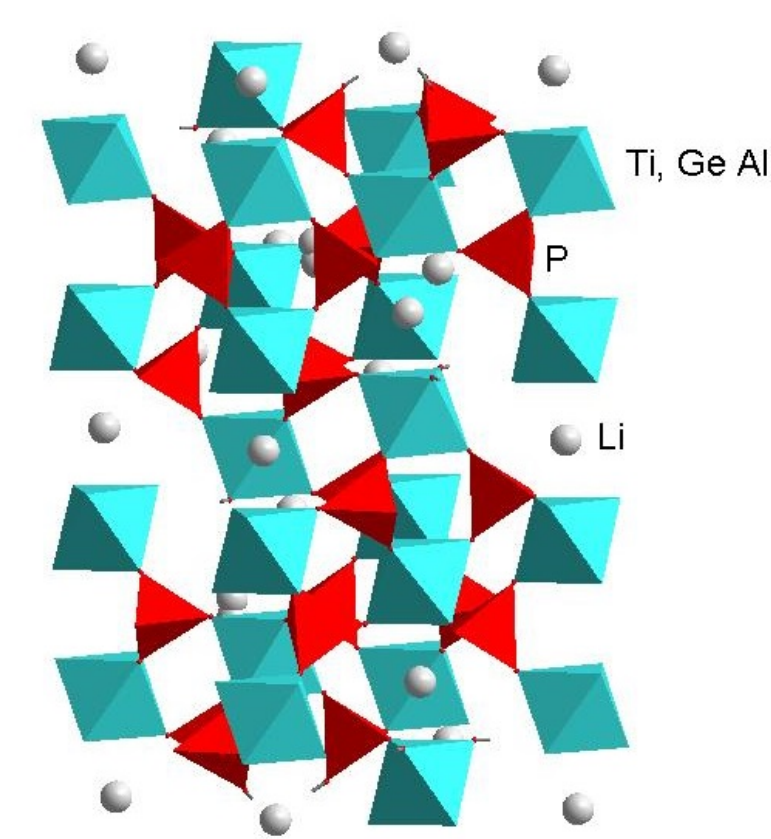
 - More resistant to high temperatures,
 - Less flammable
 - More electrochemically stable
- disadvantages:

 - Low ionic conductivity
 - Poor contact of the electrode and electrolyte

Lithium-titanium phosphates - LiTi₂(PO₄)₃
Space group R-3c; a= 8,5129 Å, c = 20,8780 Å
Ionic conductivity σ < 10⁻⁶ S/cm at 50°C

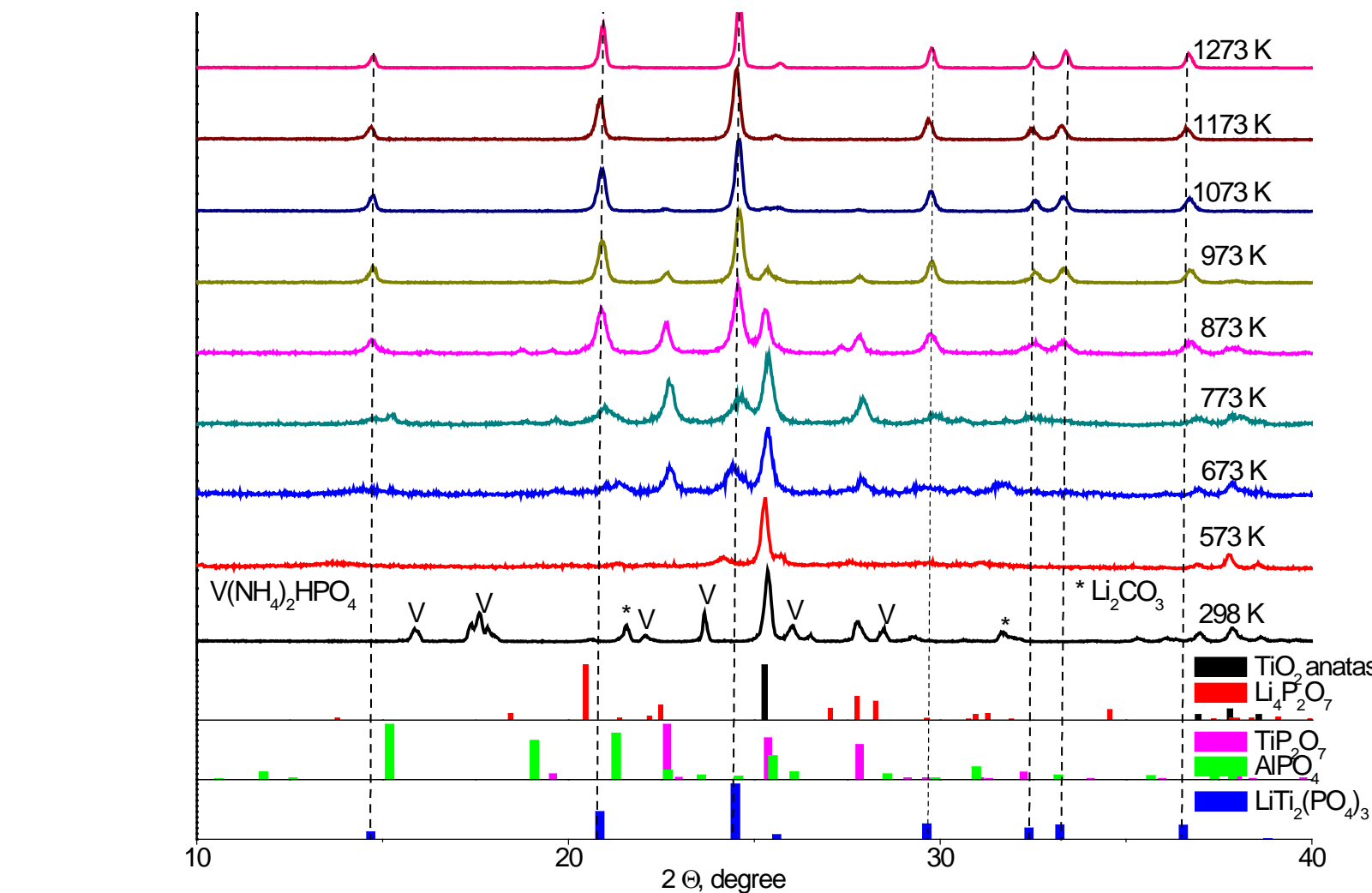
Enhancing ionic conductivity:
Iso- and heterovalent doping;

The aim of this research:
Synthesis and investigation of ionic conductivity
Li_{1+y}Ti_{2-x-y}Ge_xAl_y(PO₄)₃(y = 0-0.3)

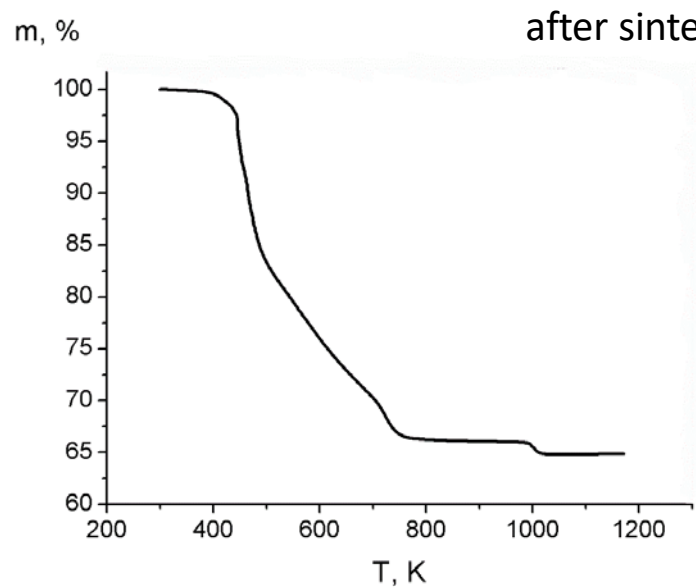


Crystal structure of Li_{1+y}Ti_{1.6}Ge_{0.2}Al_{0.2}(PO₄)₃

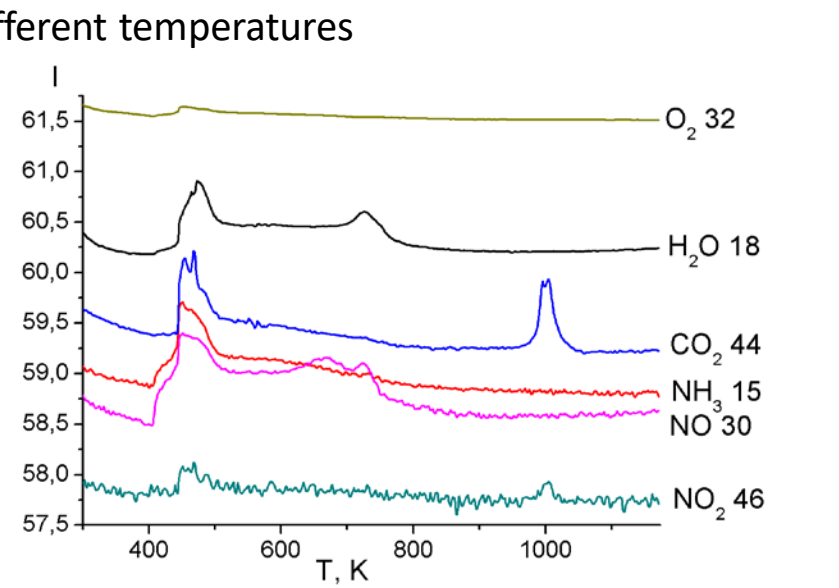
Investigation of sintering process of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃



XRD patterns of a mixture Li₂CO₃+3.2TiO₂+0.4GeO₂+0.2Al₂O₃+6(NH₄)₂HPO₄ at 298 K and after sintering for 5 h at different temperatures

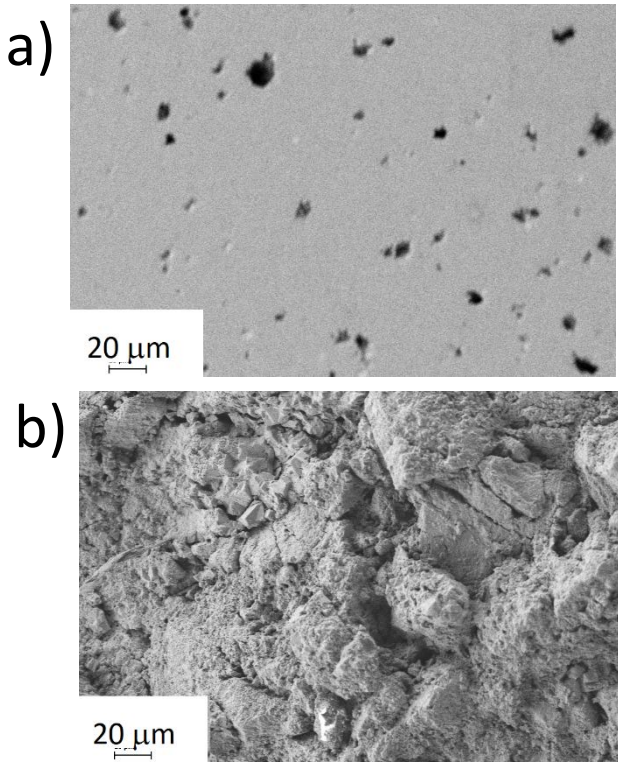
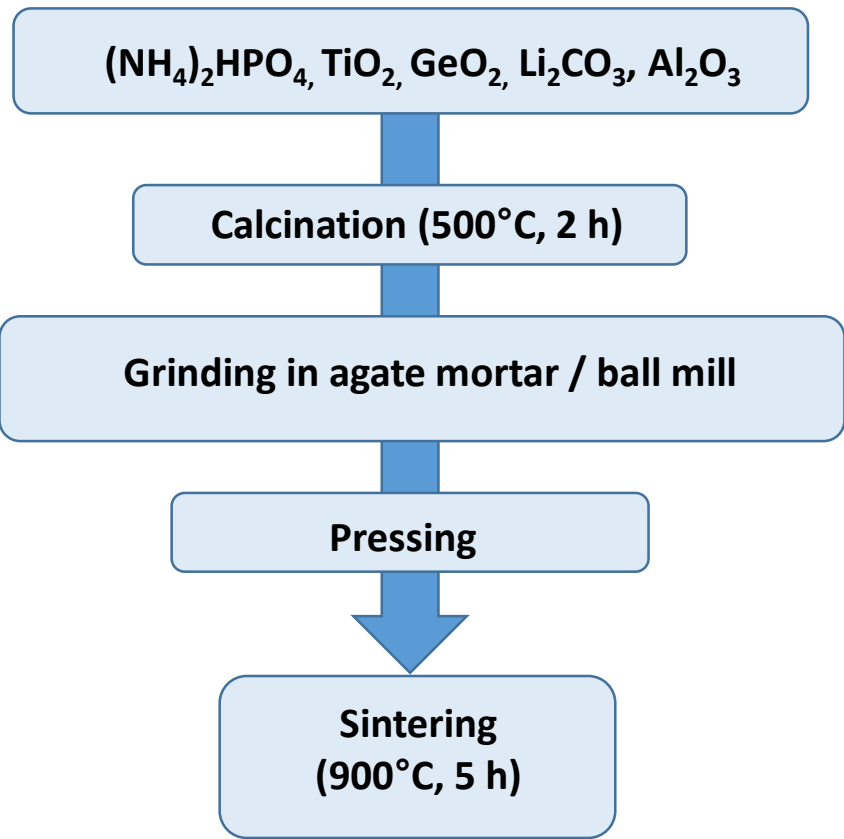


Weight loss curve of a mixture Li₂CO₃+3.2TiO₂+0.4GeO₂+0.2Al₂O₃+6(NH₄)₂HPO₄



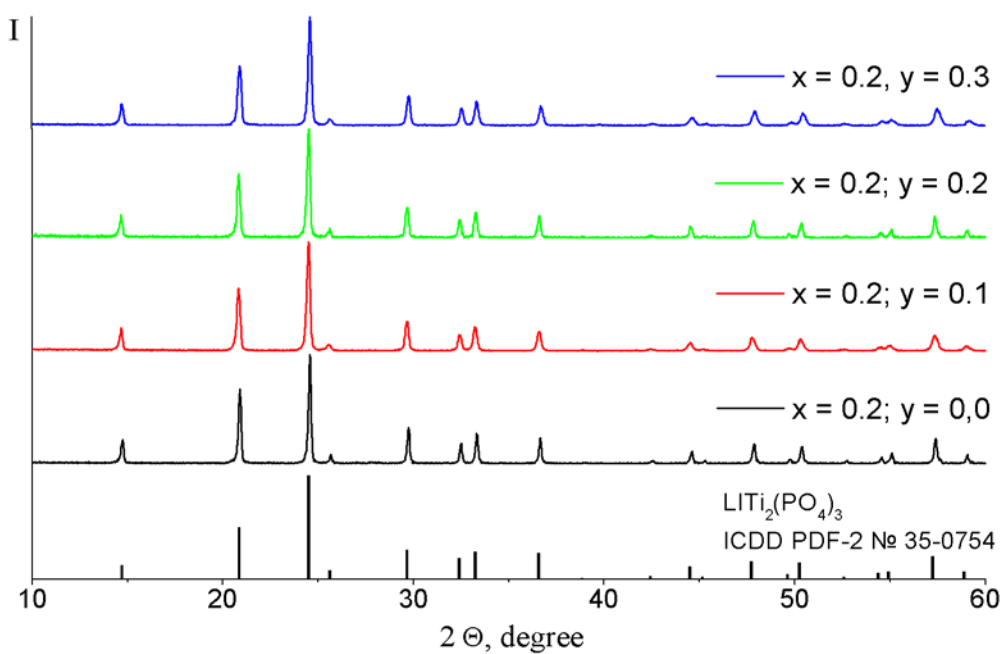
Ion currents at thermal analysis of a mixture Li₂CO₃+3.2TiO₂+0.4GeO₂+0.2Al₂O₃+6(NH₄)₂HPO₄

Synthesis scheme



SEM-images of polished pellets of Li_{1+y}Ti_{1.6}Ge_{0.2}Al_{0.2}(PO₄)₃ prepared with different modes of precursor ball-milling: a) 400 rpm, 99 cycles; b) 600 rpm, 99 cycles

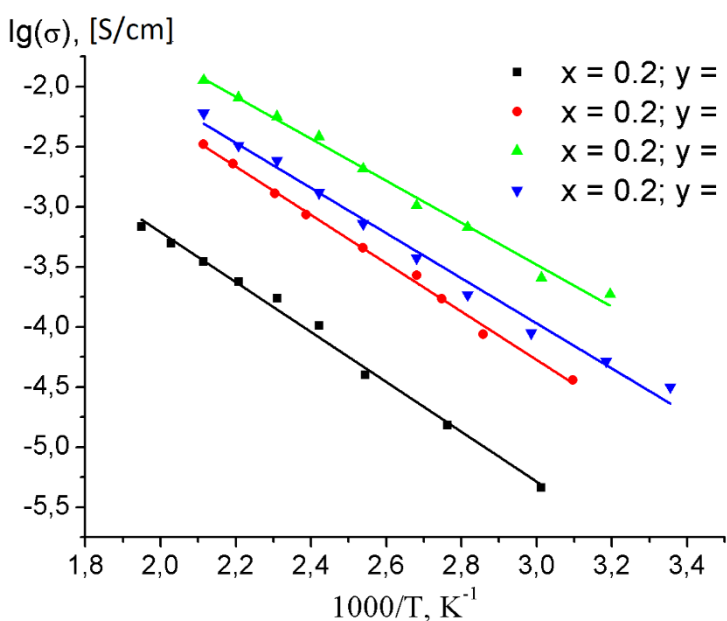
Influence of heterovalent doping of LiTi₂(PO₄)₃ on ionic conductivity



XRD patterns of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃*

Unit cell parameters of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)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)

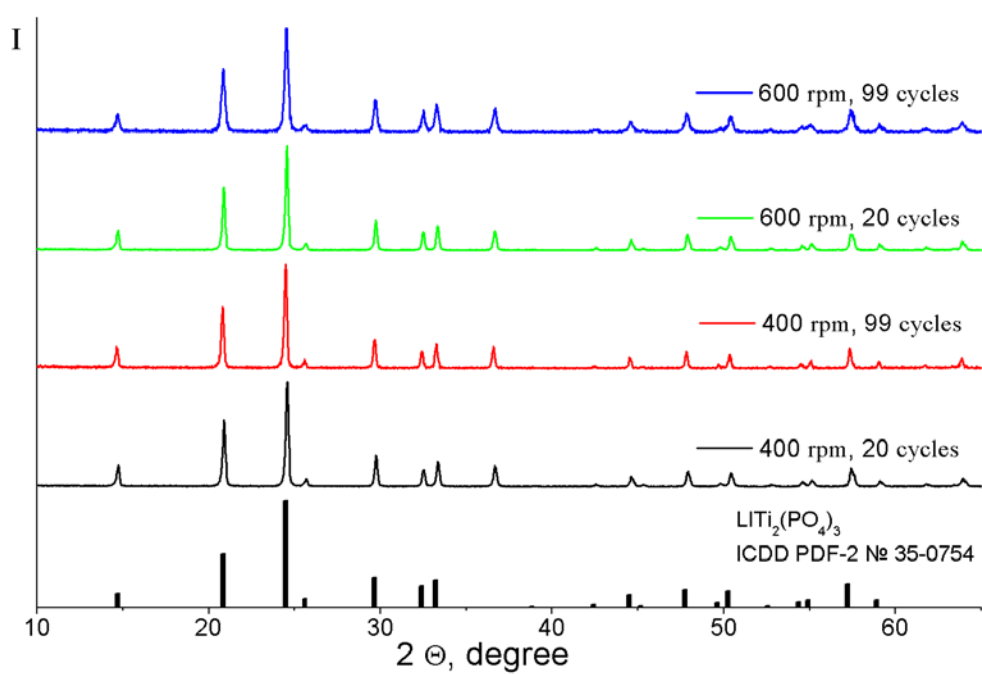


Variation of log(σ) vs 1000/T for Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃

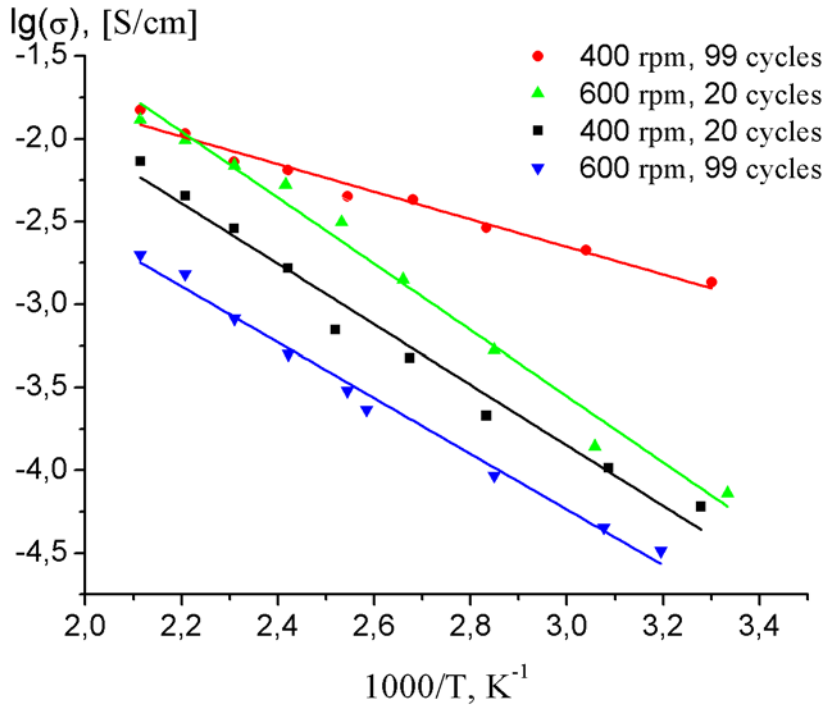
Activation energy of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃

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

Influence of precursor ball-milling on ionic conductivity of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃



XRD patterns of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃ prepared with different modes of precursor ball-milling



Plots of log(σ) vs 1000/T for Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃ prepared with different modes of precursor ball-milling

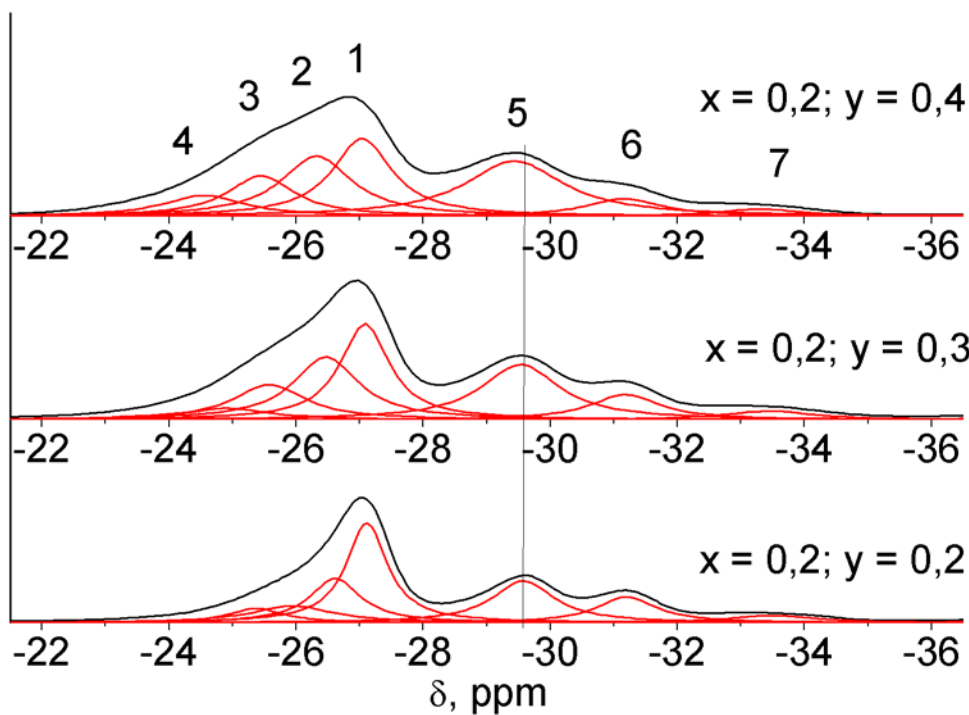
Influence different machining on parameters of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃

Rate of ball milling, rpm	Number of cycles	Pellet density, %	Conductivity (298 K), S/cm	E _a , kJ/mol
400	20	85	6,6 · 10 ⁻⁵	35 ± 2
400	99	97	1,4 · 10 ⁻³	16 ± 2
600	20	88	7,3 · 10 ⁻⁵	38 ± 2
600	99	73	3,3 · 10 ⁻⁵	32 ± 1

Conclusions:

- ✓Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃ compounds were prepared by solid state reaction and characterized by X-ray diffraction, scanning electron microscopy, ³¹P 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}(PO₄)₃ exhibits the highest ionic conductivity at room temperature (1,4·10⁻⁴ S/cm).
- ✓Detected ³¹P NMR signals have been assigned to different PO₄Ti_{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(PO₄)₃ occurs through the intermediate formation of titanium pyrophosphate.
- ✓The precursor ball-milling before the final annealing leads to a conductivity increase.

³¹P MAS NMR of Li_{1+y}Ti_{1.8-y}Ge_{0.2}Al_y(PO₄)₃



Chemical shifts of 5 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 ₄ Ti ₄	31,04	24,54	22,59	
2	PO ₄ Ti ₃ Al	16,92	22,36	20,63	
3	PO ₄ Ti ₂ Al ₂	6,93	9,08	13,07	
4	PO ₄ TiAl ₃	8,96	8,87	8,12	
5	PO ₄ Ti ₃ Ge + PO ₄ Ti ₂ GeAl	19,50	21,43	26,08	
6	PO ₄ Ti ₂ Ge ₂	11,46	8,00	6,40	
7	PO ₄ TiGe ₃	4,12	4,07	2,91	

* The highest ionic conductivity of LiTi_{2-x}Ge_x(PO₄)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